

Техническая информация

<http://doi.org/10.32864/polymmattech-2022-8-2-59-71>

УДК 541.64:547.91

КОМПОЗИТЫ ЦЕЛЛЮЛОЗА–ХИТОЗАН: ТЕНДЕНЦИИ РАЗВИТИЯ НОВЫХ ТЕХНОЛОГИЙ И ПЕРСПЕКТИВЫ ИХ ВНЕДРЕНИЯ

Т. А. САВИЦКАЯ⁺

Белорусский государственный университет, Ленинградская, 14, 220006, г. Минск, Беларусь

Цель работы — анализ современного состояния исследований в области получения композитов целлюлоза–хитозан и оценка перспектив масштабирования предлагаемых лабораторных технологий до промышленного уровня.

Приводится описание способов получения композитов целлюлоза–хитозан в виде волокон, пленок, мембран и свойств полученных продуктов. Выделено три основных метода получения композитов: поверхностная обработка целлюлозных волокон растворами или дисперсиями частиц хитозана; введение микро- или наноразмерных частиц одного полимера в раствор другого и совмещение полимеров в растворе. Показано, что в зависимости от способа получения композиционного материала совмещение целлюлозы с хитозаном осуществляется на уровне макромолекул, надмолекулярных образований и наночастиц. Предложен новый способ совмещения целлюлозы с хитозаном путем их растворения в ортофосфорной кислоте с образованием гомогенных растворов, пригодный для реализации производства композитов целлюлоза–хитозан в промышленном масштабе. Для всех остальных способов указаны причины, ограничивающие возможности их внедрения, которые обусловлены как неудовлетворительными механическими свойствами в случае получения композиционных материалов из гетерогенных многофазных систем, так и многостадийностью или нерентабельностью процесса из-за высокой стоимости растворителей в случае формования из растворов.

Ключевые слова: композиты, нанокompозиты, целлюлоза, хитозан, растворы, волокна, плёнки, мембраны.

CELLULOSE–CHITOSAN COMPOSITES: TRENDS IN THE DEVELOPMENT OF LABORATORY TECHNOLOGIES AND PROSPECTS FOR IMPLEMENTATION

T. A. SAVITSKAYA⁺

Belarusian State University, Leningradskaya St., 14, 220006, Minsk, Belarus

The purpose of this work is to analyze the current state of research in the field of obtaining cellulose–chitosan composites and to assess the prospects for scaling the proposed laboratory technologies to an industrial level.

A description is given of methods for obtaining cellulose–chitosan composites in the form of fibers, films, membranes, and the properties of the obtained products. Three main methods for obtaining composites have been identified: surface treatment of cellulose fibers with solutions or dispersions of chitosan particles; the introduction of micro- or nano-sized particles of one polymer into a solution of another and the combination of polymers in solution. It is shown that, depending on the method of obtaining a composite material, the combination of cellulose with chitosan is carried out at the level of macromolecules, supramolecular formations, and nanoparticles. A new method for combining cellulose

⁺E-mail: SavitskayaTA@bsu.by

with chitosan by dissolving them in phosphoric acid with the formation of homogeneous solutions is proposed, which is suitable for the production of cellulose–chitosan composites on an industrial scale. For all other methods, the reasons limiting the possibilities of their implementation are indicated, which are due to both unsatisfactory mechanical properties in the case of obtaining composite materials from heterogeneous multiphase systems, and the multi-stage or unprofitable process due to the high cost of solvents in the case of spinning from solutions.

Keywords: composites, nanocomposites, cellulose, chitosan, solutions, fibers, films, membranes.

Поступила в редакцию 15.04.2022

© Т. А. Савицкая, 2022

Для приобретения полного текста статьи, обращайтесь в [редакцию журнала](#)
Full text of articles can be purchased from the editorial office

Адрес редакции: ул. Кирова, 32а, 246050, г. Гомель, Беларусь
Телефон/факс: +375 (232) 34 06 36 / 34 17 11

Address: Kirov St., 32a, 246050, Gomel, Belarus
Phone: +375 (232) 34 06 36. Fax: +375 (232) 34 17 11

E-mail: polmattex@gmail.com
Web: <http://mpri.org.by/izdaniya/pmt/>

Образец цитирования:

Савицкая Т. А. Композиты целлюлоза–хитозан: тенденции развития новых технологий и перспективы их внедрения // Полимерные материалы и технологии. 2022. Т. 8, № 2. С. 59–71. <http://doi.org/10.32864/polymmattech-2022-8-2-59-71>

Citation sample:

Savitskaya T. A. Kompozity tsellyuloza–khitozan: tendentsii razvitiya novykh tekhnologiy i perspektivy ikh vnedreniya [Cellulose–chitosan composites: trends in the development of laboratory technologies and prospects for implementation]. *Polimernye materialy i tekhnologii* [Polymer Materials and Technologies], 2022, vol. 8, no. 2, pp. 59–71. <http://doi.org/10.32864/polymmattech-2022-8-2-59-71>

Литература

1. Унрод В. И., Солодовник Т. В. Хитин- и хитозансодержащие комплексы из мицелиальных грибов: получение, свойства, применение // Биополимеры і клітина, 2001. Т. 17, № 6. С. 526–531.
2. Bartnicki-Garcia S., Nickerson W. J. Isolation, composition, and structure of cell walls of filamentous and yeast-like forms of *Mucor rouxii* // Biochim. Biophys. Acta., 1962, vol. 58, pp. 102–119. doi: 10.1016/0006-3002(62)90822-3
3. Knorr D., Klein J. Production and conversion of chitosan with cultures of *mucor rouxii* or *phucomyces blakesleanus* // Biotechnol. Letters, 1986, vol. 8, is. 10, pp. 691–694. doi: 10.1007/BF01032563
4. Тихонов В. Е. Определение терминов в области хитина и хитозана // Библиотека ВНИРО [Электронный ресурс]. URL: <http://dspace.vniro.ru/handle/123456789/2121> (дата обращения: 21.12.2020).
5. Хитин и хитозан: природа, получение и применение : пер. с исп. / под ред.: В. П. Варламова, С. В. Немцева, В. Е. Тихонова. Москва : РХО, 2010. 292 с.
6. Kurita K., Sannan N., Iwakura Y. Studies on chitin, 4. Evidence for formation of block and random copolymers of N-acetyl-D-glucosamine and D-glucosamine by hetero- and homogeneous hydrolyses // Makromol. Chem., 1977, vol. 178, is. 12, pp. 3197–3202. doi: 10.1002/MACP.1977.021781203
7. Younes I., Rinaudo M. Chitin and chitosan preparation from marine sources. Structure, properties and applications // Marine Drugs, 2015, vol. 13, is. 3, pp. 1133–1174. doi: 10.3390/md13031133
8. Lévesque C. A. Fifty years of oomycetes — from consolidation to evolutionary and genomic exploration // Fungal Diversity, 2011, vol. 50, pp. 35–46. doi: 10.1007/s13225-011-0128-7
9. Sanandiya N. D., Vijay Y., Dimopoulou M., Dritsas S., Fernandez J. G. Large-scale additive manufacturing with bioinspired cellulosic materials // Sci. Rep., 2018, vol. 8. doi: 10.1038/s41598-018-26985-2
10. Роговина С. Р., Аколова Т. А., Вихорева Г. А., Горбачева И. Н., Жаров А. А., Зеленецкий А. Н. Исследование целлюлозно-хитозановых смесей, полученных в условиях сдвиговых деформаций // Высокомолекулярные соединения. Серия А. 2000. Т. 42, № 1. С. 10–15.
11. Mondal M. I. H., Ahmed F. Cellulosic fibres modified by chitosan and synthesized ecofriendly carboxymethyl chitosan from prawn shell waste // J. of Textile Inst., 2020, vol. 111, is. 1, pp. 49–59. doi: 10.1080/00405000.2019.1669321
12. Strnad S., Šauprel O., Fras-Zemljič L. Cellulose fibres functionalized by chitosan: characterization and application // Biopolymers / ed. by

- M. Elnasar. London, 2010, pp. 181–200. doi: 10.5772/10262
13. Janjic S. P., Kostić M., Vucinic V., Dimitrijević S., Popović K., Ristić M., Škundrić P. Biologically active fibers based on chitosan-coated lyocell fibers // *Carbohydrate Polymers*, 2009, vol. 78, is. 2, pp. 240–246. doi: 10.1016/j.carbpol.2009.03.033
 14. Šauperl O., Volmajer-Valh J. Viscose functionalisation with a combination of chitosan/BTCA using microwaves // *Fibres and Textiles in East. Europe*, 2013, vol. 21, no. 5, pp. 24–29.
 15. Janjic S., Kostić M., Škundrić P., Lazić B., Praskalo J. Antibacterial fibers based on cellulose and chitosan // *Contemporary Materials*, 2012, vol. 3, no. 2, pp. 207–218.
 16. Hurkins A. L., Duri S., Kloth L. C., Tran C. D. Chitosan–cellulose composite for wound dressing material. Part 2. Antimicrobial activity, blood absorption ability, and biocompatibility // *J. of Biomed. Materials Research. Part B*, 2014, vol. 102, is. 6, pp. 1199–1206. doi: 10.1002/jbm.b.33103
 17. Angtika R. S., Widiyanti P. Aminatun. Bacterial Cellulose-Chitosan-Glycerol Biocomposite as Artificial Dura Mater Candidates for Head Trauma // *J. of Biomimetics, Biomaterials and Biomed. Eng.*, 2018, vol. 36, pp. 7–16. doi: 10.4028/www.scientific.net/JBBBE.36.7
 18. Riva G. H., García-Estrada J., Vega B., López-Dellamary F., Hernández M. E., Silva J. A. Cellulose – chitosan nanocomposites – evaluation of physical, mechanical and biological properties // *Cellulose: Fundamental Aspects and Current Trends* / ed. by M. Poletto, H. L. O. Junior. Rijeca, 2015, pp. 229–251. doi: 10.5772/61727
 19. Abdul Khalil H. P. S., Chaturbhuj K. Saurabh, Adnan A. S., Nurul Fazita M. R., Syakir M. I., Davoudpour Y., Rafatullah M., Abdullah C. K., Haafiz M. K. M., Dungani R. A review on chitosan–cellulose blends and nanocellulose reinforced chitosan biocomposites: Properties and their applications // *Carbohydrate Polymers*, 2016, vol. 150, pp. 216–226. doi: 10.1016/j.carbpol.2016.05.028
 20. Fernandes S. C., Freire C. S. R., Silvestre A. J. D., Neto C. P., Gandini A. Novel materials based on chitosan and cellulose // *Polymer Intern.*, 2011, vol. 60, is. 6, pp. 875–882. doi: 10.1002/pi.3024
 21. Li Q., Zhou J., Zhang L. Structure and properties of the nanocomposite films of chitosan reinforced with cellulose whiskers // *J. of Polymer Sci. Part B: Polymer Phys.*, 2009, vol. 47, is. 11, pp. 1069–1077. doi: 10.1002/POLB.21711
 22. de Mesquita J. P., Donnici C. L., Pereira F. V. Biobased Nanocomposites from Layer-by-Layer Assembly of Cellulose Nanowhiskers with Chitosan // *Biomacromolecules*, 2010, vol. 11, no. 2, pp. 473–480. doi: 10.1021/bm9011985
 23. Cheng K., Huang C.-F., Wei Y., Hsu Sh. Novel chitosan–cellulose nanofiber self-healing hydrogels to correlate self-healing properties of hydrogels with neural regeneration effects // *NPG Asia Materials*, 2019, vol. 11, no. 1. doi: 10.1038/s41427-019-0124-z
 24. Abdul Khalil H. P. S., Chaturbhuj K. Saurabh, Adnan A. S., Nurul Fazita M. R., Syakir M. I., Davoudpour Y., Rafatullah M., Abdullah C. K., Haafiz M. K. M., Dungani R. A review on chitosan–cellulose blends and nanocellulose reinforced chitosan biocomposites: Properties and their application // *Carbohydrate Polymers*, 2016, vol. 150, pp. 216–226. doi: 10.1016/j.carbpol.2016.05.028
 25. Struszczyk H., Nousiainen P. Some aspects of viscose fibers modification by microcrystalline chitosan // *Cellulose Sources and Exploitation: Industrial Utilization, Biotechnology, and Physico-chemical Properties* / J. F. Kennedy, G. O. Phillips, P. A. Williams. New York : Ellis Horwood, 1990, pp. 177–189.
 26. Nousiainen P., Vehviläinen M., Struszczyk H., Mäkinen E. Functional hybrid fibers of cellulose/microcrystalline chitosan. I. Manufacture of viscose/microcrystalline chitosan fibers // *J. of Appl. Polymer Sci.*, 2000, vol. 76, is. 12, pp. 1725–1730. doi: 10.1002/(SICI)1097-4628(20000620)76:12<1725::AID-APP1>3.0.CO;2-1
 27. Pang F.-J., He C.-J., Wang Q.-R. Preparation and properties of cellulose/chitin blend fibers // *J. of Appl. Polymer Sci.*, 2003, vol. 90, is. 12, pp. 3430–3436. doi: 10.1002/app.13063
 28. Isogai A., Atalla R. H. Preparation of cellulose–chitosan polymer blends // *Carbohydrate Polymers*, 1992, vol. 19, is. 1, pp. 25–28. doi: 10.1016/0144-8617(92)90050-Z
 29. Hasegawa M., Isogai A., Kuga S., Onabe F. Preparation of cellulose–chitosan blend film using chloral/dimethylformamide // *Polymer*, 1994, vol. 35, is. 5, pp. 983–987. doi: 10.1016/0032-3861(94)90942-3
 30. Morgado D. L., Frollini E., Castellan A., Rosa D. S., Coma V. Biobased films prepared from NaOH/thiourea aqueous solution of chitosan and linter cellulose // *Cellulose*, 2011, vol. 18, no. 3, pp. 699–712. doi: 10.1007/s10570-011-9516-0
 31. Triverdi P., Saloranta-Simell T., Maver U., Gradišnik L., Prabhakar N., Smätt J.-H., Mohan T., Gericke M., Heinze T., Fardim P. Chitosan–cellulose multifunctional hydrogel beads: design, characterization and evaluation of cytocompatibility with breast adenocarcinoma and osteoblast cells // *Bioengineering*, 2018, vol. 5, is. 1. doi: 10.3390/bioengineering5010003
 32. Yang J., Dahlström C., Edlund H., Lindman B., Norgren M. pH-responsive cellulose–chitosan films with slow release of chitosan // *Cellulose*, 2019, vol. 26, no. 6, pp. 3763–3776. doi: 10.1007/s10570-019-02357-5
 33. Kim U.-J., Kimura S., Wada M. Characterization of cellulose–chitosan gels prepared using a LiOH/urea aqueous solution // *Cellulose*, 2019, vol. 26, no. 10, pp. 6189–6199. doi: 10.1007/s10570-019-02527-5
 34. Meng G., Peng H., Wu J., Wang Y., Wang H., Liu Z., Guo X. Fabrication of superhydrophobic cellulose/chitosan composite aerogel for oil/water separation // *Fiber and Polymers*, 2017, vol. 18, no. 4, pp. 706–712. doi: 10.1007/s12221-017-1099-4
 35. Yang J., Kwon G.-J., Hwang K., Kim D.-Y. Cellulose–Chitosan antibacterial composite films prepared from LiBr solution // *Polymers*, 2018, vol. 10, no. 10, pp. 1058–1064. doi: 10.3390/polym10101058
 36. Lin S., Chen L., Huang L., Cao S., Luo X., Liu K., Huang Z. Preparation and characterization of chitosan/cellulose blend films using ZnCl₂·3H₂O as a solvent // *BioResources*, 2012, vol. 7, no. 4, pp. 5488–5499.
 37. Kuzmina O., Heinze T., Wawro D. Blending of cellulose and chitosan in alkyl imidazolium ionic liquids // *International Scholarly Research Notices*, 2012. doi: 10.5402/2012/251950
 38. Муравьев А. А. Растворы смесей целлюлозы и хитина в ионных жидкостях и композиционные материалы на их основе : автореф. дис. канд. хим. наук : 02.00.06; 02.00.04. СПб., 2017. 23 с.
 39. Lv Y., Wu J., Zhang J., Niu Y., Liu C.-Y., He J., Zhang J. Rheological properties of cellulose/ionic liquid/dimethylsulfoxide (DMSO) solutions // *Polymer*, 2012, vol. 53, is. 12, pp. 2524–2531. doi: 10.1016/j.polymer.2012.03.037
 40. Fu R., Ji X., Ren Y., Wang G., Cheng B. Antibacterial blend films of cellulose and chitosan prepared from binary ionic liquid system // *Fibers and Polymers*, 2017, vol. 18, pp. 852–858. doi: 10.1007/s12221-017-1130-9
 41. Rogovina C. Z., Golova L. K., Borodina O. E., Vikhoreva G. A. Chitosan–cellulose films fabricated from mixtures of polysaccharides in N-methylmorpholine N-oxide // *Fiber Chemistry*, 2012, vol. 34, pp. 18–20. doi: 10.1023/A:1015547105887
 42. Janjic S., Kostić M., Škundrić P., Lazić B., Praskalo J. Antibacterial fibers based on cellulose and chitosan // *Contemporary Materials*, 2012, vol. 3, no. 2, pp. 207–218.
 43. Wendler F., Meister F., Wawro D., Wesolowska E., Ciechańska D., Saake B., Puls J., Le Moigne N., Navard P. Polysaccharide blend fibres formed from NaOH, N-methylmorpholine-N-oxide and 1-ethyl-3-methylimidazolium acetate // *Fibres and Textiles in East. Europe*, 2010, vol. 18, no. 2, pp. 21–30.
 44. Biodegradable and sustainable fibres / ed. by R. S. Blackburn. Cambridge : Woodhead, 2005. 546 p.
 45. Parmar M. S., Sisodia N., Sonee N. Comparative Study on Dyeing Behavior of Crabony and Viscose Rayon Fibres // *Intern. J. of Eng. Research and Technol.*, 2013, vol. 2, is. 12, pp. 2321–2328.

46. Гриншпан Д. Д., Гончар А. Н., Савицкая Т. А., Цыганкова Н. Г., Макаревич С. Е. Получение гидратцеллюлозных волокон из растворов целлюлозы в ортофосфорной кислоте // Вес. Нац. акад. наук Беларуси. Сер. хім. навук, 2014. № 2. С. 115–118.
47. Hanchar A., Tsygankova N., Makarevich S., Sheima E., Savitskaya T., Grinshpan D. New solution of the old problem: phosphoric acid for the cellulose fiber production // IMTEX'2011 : proceedings of the XI International conference, Lodz, 7–8 Nov. 2011 / red. R. Korycki. Lodz, 2011, pp. 47–52.
48. Grinshpan D., Savitskaya T., Tsygankova N., Makarevich S., Hanchar A. Will the cellulose fiber production become greener? // IMTEX'2011 : proceedings of the XI International conference, Lodz, 7–8 Nov. 2011 / red. R. Korycki. Lodz, 2011, pp. 59–64.
49. Гриншпан Д. Д., Цыганкова Н. Г., Макаревич С. Е., Савицкая Т. А., Серебряков Г. Ф., Вовк В. И., Кудрявцева Т. Н., Белоглазов А. П. Самозатухающие волокна и их композиционные материалы на основе целлюлозы и хитозана // Нефтехимический комплекс. Приложение к журналу «Вестник Белнефтехима», 2017. № 1. С. 13–15.
50. Гриншпан Д. Д., Цыганкова Н. Г., Макаревич С. Е., Савицкая Т. А., Кудрявцева Т. Н., Белоглазов А. П. Самозатухающие волокна и текстильные материалы на основе целлюлозы и хитозана // Полимерные материалы пониженной горючести : сборник тезисов докладов IX Международной конференции, [г. Минск, 20–24 мая 2019 г.]. Минск, 2019. С. 38–40.
51. Гриншпан Д. Д., Гончар А. Н., Цыганкова Н. Г., Савицкая Т. А., Макаревич С. Е. Разработка технологии получения самозатухающего композитного целлюлозно-хитозанового волокна // Полимерные композиты и трибология (Поликомтриб-2015) : тез. докл. междунар. науч.-техн. конф., Гомель, 23–26 июня 2015 г. / Нац. акад. наук Беларуси [и др.]; редкол.: В. Н. Адериха [и др.]. Гомель, 2015. С. 111.
52. Conte P., Maccotta A., De Pasquale C., Bubici S., Alonzo G. Dissolution mechanism of crystalline cellulose in H₃PO₄ as assessed by high-field NMR spectroscopy and fast field cycling NMR relaxometry // J. of Agr. Food Chem., 2009, vol. 57, is. 19, pp. 8748–8752. doi: 10.1021/jf9022146
53. Boerstol H., Maatman J., Westerink B., Koenders B. M. Liquid crystalline solutions of cellulose in phosphoric acid // Polymer, 2001, vol. 42, is. 17, pp. 7371–7379. doi: 10.1016/S0032-3861(01)00210-5
54. Northolt M. G., Boerstol H., Maatman H., Huisman R., Elzerman H. The structure and properties of cellulose fibres spun from an anisotropic phosphoric acid solution // Polymer, 2001, vol. 42, is. 19, pp. 8249–8264. doi: 10.1016/S0032-3861(01)00211-7
55. Кочетков С. П., Смирнов Н. Н., Ильин А. П. Концентрирование и очистка экстракционной фосфорной кислоты. Иваново : ИГХТУ, 2007. 304 с.
56. Grinshpan D. D., Gonchar A. N., Tsygankova N. G., Makarevich S. E., Savitskaya T. A., Sheimo E. V. Rheological properties of concentrated solutions of cellulose and its mixtures with other polymers in orthophosphoric acid // J. Eng. Phys. Thermophys., 2011, vol. 84, pp. 594–598. doi.org/10.1007/s10891-011-0510-z
57. Savitskaya T., Hanchar A., Tsygankova N., Makarevich S., Grinshpan D. Cellulose polymer blends fibers: production processes and properties // IMTEX'2011 : proceedings of the XI International conference, Lodz, 7–8 Nov. 2011 / red. R. Korycki. Lodz, 2011, pp. 77–82.
58. Savitskaya T., Hrynschan D. New chemical materials and education products developed according to “green” chemistry principles in the Belarusian state university // Наука. Инновации. Производство = Science. Innovation. Production : сб. материалов Белорусско-Корейского форума, Минск, 27 июня 2011 г. Minsk : BNTU, 2011, pp. 51–52.
59. Гриншпан Д. Д., Гончар А. Н., Савицкая Т. А., Цыганкова Н. Г., Макаревич С. Е. Реологические свойства систем целлюлоза-хитозан-ортофосфорная кислота в различных фазовых состояниях // Высокомолекулярные соединения. Сер. А., 2014. Т. 56, № 2. С. 142–151. doi: 10.7868/S2308112014020059
60. Гриншпан Д. Д., Гончар А. Н., Савицкая Т. А., Цыганкова Н. Г., Макаревич С. Е. Формирование ориентационно-упорядоченных структур в растворах и пленках смесей целлюлозы с хитозаном // Весці Нац. акад. навук Беларусі. Сер. хім. навук, 2014. № 1. С. 96–100.
61. Grinshpan D., Savitskaya T., Tsygankova N., Makarevich S., Kimlenka I., Ivashkevich O. Good real word examples of wood-based sustainable chemistry // Sustainable Chem. and Pharm., 2017, vol. 5, pp. 1–13. doi: 10.1016/j.scp.2016.11.001
62. Савицкая Т. А., Гриншпан Д. Д., Цыганкова Н. Г., Невар Т. Н., Гончар А. Н., Резников И. В., Тельшева Г. М., Аржаница А. С., Дижбите Т. Н. Композитное биотопливо и удобрения на основе гидролизного лигнина // Наука, инновации, инвестиции : сборник материалов белорусско-латвийского форума. 2014 [Электронный ресурс]. URL: <http://old.bntu.by/images/stories/News/Forum/Latvia2013/21.pdf> (дата обращения: 02.10.2020).
63. Савицкая Т. А., Цыганкова Н. Г., Макаревич С. Е., Гриншпан Д. Д. «Зелёная» химия в новых технологиях переработки целлюлозы и лигнина // Химия и химическая технология переработки растительного сырья : материалы докл. Междунар. науч.-техн. конф., посвящ. 100-лет. со дня рожд. проф. В. М. Резникова, 10–12 окт. 2018 г. / редкол.: И. В. Войтов (гл. ред.) [и др.]. Минск, 2018. С. 15–19.

References

1. Unrod V. I., Solodovnik T. V. Chitin- i khitozansoderzhashchie kompleksy iz mitselial'nykh gribov: poluchenie, svoystva, primeneniye [Chitin- and chitosan-containing complexes from filamentous fungi: preparation, properties, application]. *Biopolimeri i khitina* [Biopolymers and Cell], 2001, vol. 17, no. 6, pp. 526–531.
2. Bartnicki-Garcia S., Nickerson W. J. Isolation, composition, and structure of cell walls of filamentous and yeast-like forms of *Mucor rouxii*. *Biochim. Biophys. Acta.*, 1962, vol. 58, pp. 102–119. doi: 10.1016/0006-3002(62)90822-3
3. Knorr D., Klein J. Production and conversion of chitosan with cultures of *mucor rouxii* or *phucomyces blakesleeanus*. *Biotechnol. Letters*, 1986, vol. 8, is. 10, pp. 691–694. doi: 10.1007/BF01032563
4. Tikhonov V. E. Opredeleniye terminov v oblasti khitina i khitozana [Definition of terms in the field of chitin and chitosan]. Available at: <http://dspace.vniro.ru/handle/123456789/2121> (accessed 21.12.2020).
5. *Khitin i khitozan: priroda, poluchenie i primeneniye* [Chitin and chitosan: nature, production, application]. Eds.: V. P. Varlamov, S. V. Nemtsev, V. E. Tikhonov. Moscow : RKhO Publ., 2010. 292 p.
6. Kurita K., Sannan N., Iwakura Y. Studies on chitin, 4. Evidence for formation of block and random copolymers of N-acetyl-D-glucosamine and D-glucosamine by hetero- and homogeneous hydrolyses. *Makromol. Chem.*, 1977, vol. 178, is. 12, pp. 3197–3202. doi: 10.1002/MACP.1977.021781203
7. Younes I., Rinaudo M. Chitin and chitosan preparation from marine sources. Structure, properties and applications. *Marine Drugs*, 2015, vol. 13, is. 3, pp. 1133–1174. doi: 10.3390/md13031133
8. Lévesque C. A. Fifty years of oomycetes — from consolidation to evolutionary and genomic exploration. *Fungal Diversity*, 2011, vol. 50, pp. 35–46. doi: 10.1007/s13225-011-0128-7
9. Sanandiya N. D., Vijay Y., Dimopoulou M., Dritsas S., Fernandez J. G. Large-scale additive manufacturing with bioinspired cellulosic materials. *Sci. Rep.*, 2018, vol. 8. doi: 10.1038/s41598-018-26985-2
10. Rogovina C. P., Akopova T. A., Vikhoreva G. A., Gorbacheva I. N., Zharov A. A., Zelenetskiy A. N. Issledovanie tsellyulozno-khitozanovykh smesey, poluchennykh v usloviyakh sdvigovykh deformatsiy [Study of cellulose-chitosan mixtures obtained under shear

- conditions). *Vysokomolekulyarnye soedineniya. Seriya A* [Polymer Science: Series A – Polymer Physics], 2000, vol. 42, no. 1, pp. 10–15.
11. Mondal M. I. H., Ahmed F. Cellulosic fibres modified by chitosan and synthesized ecofriendly carboxymethyl chitosan from prawn shell waste. *J. of Textile Inst.*, 2020, vol. 111, is. 1, pp. 49–59. doi: 10.1080/00405000.2019.1669321
 12. Strnad S., Šauperl O., Fras-Zemljic L. Cellulose fibres functionalized by chitosan: characterization and application. *Biopolymers*. Ed. M. Elnasar. London, 2010, pp. 181–200. doi: 10.5772/10262
 13. Janjic S. P., Kostic M., Vucinic V., Dimitrijevic S., Popovic K., Ristic M., Škundric P. Biologically active fibers based on chitosan-coated lyocell fibers. *Carbohydrate Polymers*, 2009, vol. 78, is. 2, pp. 240–246. doi: 10.1016/j.carbpol.2009.03.033
 14. Šauperl O., Volmajer-Valh J. Viscose functionalisation with a combination of chitosan/BTCA using microwaves. *Fibres and Textiles in East Europe*, 2013, vol. 21, no. 5, pp. 24–29.
 15. Janjic S., Kostic M., Škundric P., Lazić B., Praskalo J. Antibacterial fibers based on cellulose and chitosan. *Contemporary Materials*, 2012, vol. 3, no. 2, pp. 207–218.
 16. Hurkins A. L., Duri S., Kloth L. C., Tran C. D. Chitosan–cellulose composite for wound dressing material. Part 2. Antimicrobial activity, blood absorption ability, and biocompatibility. *J. of Biomed. Materials Research. Part B*, 2014, vol. 102, is. 6, pp. 1199–1206. doi: 10.1002/jbm.b.33103
 17. Angtika R. S., Widiyanti P. Aminatun. Bacterial Cellulose-Chitosan-Glycerol Biocomposite as Artificial Dura Mater Candidates for Head Trauma. *J. of Biomimetics, Biomaterials and Biomed. Eng.*, 2018, vol. 36, pp. 7–16. doi: 10.4028/www.scientific.net/JBBBE.36.7
 18. Riva G. H., García-Estrada J., Vega B., López-Dellamary F., Hernández M. E., Silva J. A. Cellulose – chitosan nanocomposites – evaluation of physical, mechanical and biological properties. *Cellulose: Fundamental Aspects and Current Trends*. Eds.: M. Poletto, H. L. O. Junior. Rijeca, 2015, pp. 229–251. doi: 10.5772/61727
 19. Abdul Khalil H. P. S., Chaturbhuj K. Saurabh, Adnan A. S., Nurul Fazita M. R., Syakir M. I., Davoudpour Y., Rafatullah M., Abdullah C. K., Haafiz M. K. M., Dungani R. A review on chitosan-cellulose blends and nanocellulose reinforced chitosan biocomposites: Properties and their applications. *Carbohydrate Polymers*, 2016, vol. 150, pp. 216–226. doi: 10.1016/j.carbpol.2016.05.028
 20. Fernandes S. C., Freire C. S. R., Silvestre A. J. D., Neto C. P., Gandini A. Novel materials based on chitosan and cellulose. *Polymer Intern.*, 2011, vol. 60, is. 6, pp. 875–882. doi: 10.1002/pi.3024
 21. Li Q., Zhou J., Zhang L. Structure and properties of the nanocomposite films of chitosan reinforced with cellulose whiskers. *J. of Polymer Sci. Part B: Polymer Phys.*, 2009, vol. 47, is. 11, pp. 1069–1077. doi: 10.1002/POLB.21711
 22. de Mesquita J. P., Donnici C. L., Pereira F. V. Biobased Nanocomposites from Layer-by-Layer Assembly of Cellulose Nanowhiskers with Chitosan. *Biomacromolecules*, 2010, vol. 11, no. 2, pp. 473–480. doi: 10.1021/bm9011985
 23. Cheng K., Huang C.-F., Wei Y., Hsu Sh. Novel chitosan-cellulose nanofiber self-healing hydrogels to correlate self-healing properties of hydrogels with neural regeneration effects. *NPG Asia Materials*, 2019, vol. 11, no. 1. doi: 10.1038/s41427-019-0124-z
 24. Abdul Khalil H. P. S., Chaturbhuj K. Saurabh, Adnan A. S., Nurul Fazita M. R., Syakir M. I., Davoudpour Y., Rafatullah M., Abdullah C. K., Haafiz M. K. M., Dungani R. A review on chitosan–cellulose blends and nanocellulose reinforced chitosan biocomposites: Properties and their application. *Carbohydrate Polymers*, 2016, vol. 150, pp. 216–226. doi: 10.1016/j.carbpol.2016.05.028
 25. Struszczyk H., Nousiainen P. Some aspects of viscose fibers modification by microcrystalline chitosan. *Cellulose Sources and Exploitation: Industrial Utilization, Biotechnology, and Physico-chemical Properties* / J. F. Kennedy, G. O. Phillips, P. A. Williams. New York : Ellis Horwood, 1990, pp. 177–189.
 26. Nousiainen P., Vehviläinen M., Struszczyk H., Mäkinen E. Functional hybrid fibers of cellulose/microcrystalline chitosan. I. Manufacture of viscose/microcrystalline chitosan fibers. *J. of Appl. Polymer Sci.*, 2000, vol. 76, is. 12, pp. 1725–1730. doi: 10.1002/(SICI)1097-4628(20000620)76:12<1725::AID-APP1>3.0.CO;2-1
 27. Pang F.-J., He C.-J., Wang Q.-R. Preparation and properties of cellulose/chitin blend fibers. *J. of Appl. Polymer Sci.*, 2003, vol. 90, is. 12, pp. 3430–3436. doi: 10.1002/app.13063
 28. Isogai A., Atalla R. H. Preparation of cellulose-chitosan polymer blends. *Carbohydrate Polymers*, 1992, vol. 19, is. 1, pp. 25–28. doi: 10.1016/0144-8617(92)90050-Z
 29. Hasegawa M., Isogai A., Kuga S., Onabe F. Preparation of cellulose-chitosan blend film using chloral/dimethylformamide. *Polymer*, 1994, vol. 35, is. 5, pp. 983–987. doi: 10.1016/0032-3861(94)90942-3
 30. Morgado D. L., Frollini E., Castellan A., Rosa D. S., Coma V. Biobased films prepared from NaOH/thiourea aqueous solution of chitosan and linter cellulose. *Cellulose*, 2011, vol. 18, no. 3, pp. 699–712. doi: 10.1007/s10570-011-9516-0
 31. Triverdi P., Saloranta-Simell T., Maver U., Gradišnik L., Prabhakar N., Smätt J.-H., Mohan T., Gericke M., Heinze T., Fardim P. Chitosan-cellulose multifunctional hydrogel beads: design, characterization and evaluation of cytocompatibility with breast adenocarcinoma and osteoblast cells. *Bioengineering*, 2018, vol. 5, is. 1. doi: 10.3390/bioengineering5010003
 32. Yang J., Dahlström C., Edlund H., Lindman B., Norgren M. pH-responsive cellulose-chitosan films with slow release of chitosan. *Cellulose*, 2019, vol. 26, no. 6, pp. 3763–3776. doi: 10.1007/s10570-019-02357-5
 33. Kim U.-J., Kimura S., Wada M. Characterization of cellulose–chitosan gels prepared using a LiOH/urea aqueous solution. *Cellulose*, 2019, vol. 26, no. 10, pp. 6189–6199. doi: 10.1007/s10570-019-02527-5
 34. Meng G., Peng H., Wu J., Wang Y., Wang H., Liu Z., Guo X. Fabrication of superhydrophobic cellulose/chitosan composite aerogel for oil/water separation. *Fiber and Polymers*, 2017, vol. 18, no. 4, pp. 706–712. doi: 10.1007/s12221-017-1099-4
 35. Yang J., Kwon G.-J., Hwang K., Kim D.-Y. Cellulose-Chitosan antibacterial composite films prepared from LiBr solution. *Polymers*, 2018, vol. 10, no. 10, pp. 1058–1064. doi: 10.3390/polym10101058
 36. Lin S., Chen L., Huang L., Cao S., Luo X., Liu K., Huang Z. Preparation and characterization of chitosan/cellulose blend films using ZnCl₂·3H₂O as a solvent. *BioResources*, 2012, vol. 7, no. 4, pp. 5488–5499.
 37. Kuzmina O., Heinze T., Wawro D. Blending of cellulose and chitosan in alkyl imidazolium ionic liquids. *International Scholarly Research Notices*, 2012. doi: 10.5402/2012/251950
 38. Murav'ev A. A. Rastvory smesey tsellyulozy i khitina v ionnykh zhidkostyakh i kompozitsionnye materialy na ikh osnove. Avtoref. dis. kand. khim. Nauk [Solutions of mixtures of cellulose and chitin in ionic liquids and composite materials based on them. PhD chem. sci. abstract diss.]. Saint-Petersburg, 2017. 23 p.
 39. Lv Y., Wu J., Zhang J., Niu Y., Liu C.-Y., He J., Zhang J. Rheological properties of cellulose/ionic liquid/dimethylsulfoxide (DMSO) solutions. *Polymer*, 2012, vol. 53, is. 12, pp. 2524–2531. doi: 10.1016/j.polymer.2012.03.037
 40. Fu R., Ji X., Ren Y., Wang G., Cheng B. Antibacterial blend films of cellulose and chitosan prepared from binary ionic liquid system. *Fibers and Polymers*, 2017, vol. 18, pp. 852–858. doi: 10.1007/s12221-017-1130-9
 41. Rogovina C. Z., Golova L. K., Borodina O. E., Vikhoreva G. A. Chitosan–cellulose films fabricated from mixtures of polysaccharides in N-methylmorpholine N-oxide. *Fiber Chemistry*, 2012, vol. 34, pp. 18–20. doi: 10.1023/A:1015547105887
 42. Janjic S., Kostic M., Škundric P., Lazić B., Praskalo J. Antibacterial fibers based on cellulose and chitosan. *Contemporary Materials*, 2012, vol. 3, no. 2, pp. 207–218.
 43. Wendler F., Meister F., Wawro D., Wesolowska E., Ciechańska D., Saake B., Puls J., Le Moigne N., Navard P. Polysaccharide blend

- fibres formed from NaOH, N-methylmorpholine-N-oxide and 1-ethyl-3-methylimidazolium acetate. *Fibres and Textiles in East. Europe*, 2010, vol. 18, no. 2, pp. 21–30.
44. *Biodegradable and sustainable fibres*. Ed. by R. S. Blackburn. Cambridge : Woodhead, 2005. 546 p.
 45. Parmar M. S., Sisodia N., Sonee N. Comparative Study on Dyeing Behavior of Crabyon and Viscose Rayon Fibres. *Intern. J. of Eng. Research and Technol.*, 2013, vol. 2, is. 12, pp. 2321–2328.
 46. Grinshpan D. D., Gonchar A. N., Savitskaya T. A., Tsygankova N. G., Makarevich S. E. Poluchenie gidratsellyuloznykh volokon iz rastvorov tsellyulozy v ortofosfornoy kislyote [Preparation of hydrated cellulose fibers from solutions of cellulose in phosphoric acid]. *Vesti Natsional'noy akademii nauk Belarusi. Seriya himicheskikh nauk* [Proceedings of the National Academy of Sciences of Belarus, Chemical Series], 2014, no. 2, pp. 115–118.
 47. Hanchar A., Tsygankova N., Makarevich S., Sheima E., Savitskaya T., Grinshpan D. New solution of the old problem: phosphoric acid for the cellulose fiber production. *Proceedings of the XI International conference "IMTEX'2011"*. Ed. R. Korycki. Lodz, 2011, pp. 47–52.
 48. Grinshpan D., Savitskaya T., Tsygankova N., Makarevich S., Hanchar A. Will the cellulose fiber production become greener? *Proceedings of the XI International conference "IMTEX'2011"*. Ed. R. Korycki. Lodz, 2011, pp. 59–64.
 49. Grinshpan D. D., Tsygankova N. G., Makarevich S. E., Savitskaya T. A., Serebryakov G. F., Vovk V. I., Kudryavtseva T. N., Beloglazov A. P. Samozatukhayushchie volokna i ikh kompozitsionnye materialy na osnove tsellyulozy i khitozana [Self-extinguishing fibers and their composite materials based on cellulose and chitosan]. *Neftekhimicheskii kompleks* [Petrochemical Complex], 2017, no. 1, pp. 13–15.
 50. Grinshpan D. D., Tsygankova N. G., Makarevich S. E., Savitskaya T. A., Kudryavtseva T. N., Beloglazov A. P. Samozatukhayushchie volokna i tekstil'nye materialy na osnove tsellyulozy i khitozana [Self-extinguishing fibers and textile materials based on cellulose and chitosan]. *Sbornik tezisev dokladov IX Mezhdunarodnoy konferentsii «Polimernye materialy ponizhennoj gorjuchesti»* [Materials of the IX International Conference "Polymer materials of low combustibility"]. Minsk, 2019, pp. 38–40.
 51. Grinshpan D. D., Gonchar A. N., Tsygankova N. G., Savitskaya T. A., Makarevich S. E. Razrabotka tekhnologii polucheniya samozatukhayushchego kompozitnogo tsellyulozno-khitozanovogo volokna [Development of technology for obtaining self-extinguishing composite cellulose-chitosan fiber]. *Tezisy dokladov Mezhdunarodnoy nauchno-tekhnicheskoy konferentsii «Polimernye kompozity i tribologiya» (Polikomtrib-2015)* [Abstracts of the International Scientific and Technical Conference "Polymer composites and tribology"]. Gomel', 2015, pp. 111.
 52. Conte P., Maccotta A., De Pasquale C., Bubici S., Alonzo G. Dissolution mechanism of crystalline cellulose in H₃PO₄ as assessed by high-field NMR spectroscopy and fast field cycling NMR relaxometry. *J. of Agr. Food Chem.*, 2009, vol. 57, is. 19, pp. 8748–8752. doi: 10.1021/jf9022146
 53. Boerstol H., Maatman J., Westerink B., Koenders B. M. Liquid crystalline solutions of cellulose in phosphoric acid. *Polymer*, 2001, vol. 42, is. 17, pp. 7371–7379. doi: 10.1016/S0032-3861(01)00210-5
 54. Northolt M. G., Boerstol H., Maatman H., Huisman R., Veurink J., Elzerman H. The structure and properties of cellulose fibres spun from an anisotropic phosphoric acid solution. *Polymer*, 2001, vol. 42, is. 19, pp. 8249–8264. doi: 10.1016/S0032-3861(01)00211-7
 55. Kochetkov S. P., Smirnov N. N., Il'in A. P. *Kontsentrirovaniye i oshistka ekstraktsionnoy fosfornoy kisloty* [Concentration and purification of extractive phosphoric acid]. Ivanovo : IGKhTU Publ., 2007. 304 p.
 56. Grinshpan D. D., Gonchar A. N., Tsygankova N. G., Makarevich S. E., Savitskaya T. A., Sheimo E. V. Rheological properties of concentrated solutions of cellulose and its mixtures with other polymers in orthophosphoric acid. *J. Eng. Phys. Thermophys.*, 2011, vol. 84, pp. 594–598. doi.org/10.1007/s10891-011-0510-z
 57. Savitskaya T., Hanchar A., Tsygankova N., Makarevich S., Grinshpan D. Cellulose polymer blends fibers: production processes and properties. *Proceedings of the XI International conference "IMTEX'2011"*. Ed. R. Korycki. Lodz, 2011, pp. 77–82.
 58. Savitskaya T., Hrynshpan D. New chemical materials and education products developed according to "green" chemistry principles in the Belarusian state university. *Sbornik materialov Belorussko-Koreyskogo foruma «Nauka. Innovatsii. Proizvodstvo»* [Collection of materials of the Belarusian-Korean forum "Science. Innovation. Production"]. Minsk : BNTU Publ., 2011, pp. 51–52.
 59. Grinshpan D. D., Gonchar A. N., Savitskaya T. A., Tsygankova N. G., Makarevich S. E. Reologicheskie svoystva sistem tsellyuloza-khitozan-ortofosfornaya kislyota v razlichnykh fazovykh sostoyaniyakh [Rheological properties of cellulose-chitosan-orthophosphoric acid systems in various phase states]. *Vysokomolekulyarnye soedineniya. Seriya A* [Polymer Science: Series A - Polymer Physics], 2014, vol. 56, no. 2, pp. 142–151. doi: 10.7868/S2308112014020059
 60. Grinshpan D. D., Gonchar A. N., Savitskaya T. A., Tsygankova N. G., Makarevich S. E. Formirovaniye orientatsionno-uporyadochennykh struktur v rastvorakh i plenkakh smesey tsellyulozy s khitozanom [Formation of orientationally ordered structures in solutions and films of mixtures of cellulose with chitosan]. *Vesti Natsional'noy akademii nauk Belarusi. Seriya himicheskikh nauk* [Proceedings of the National Academy of Sciences of Belarus, Chemical Series], 2014, no. 1, pp. 96–100.
 61. Grinshpan D., Savitskaya T., Tsygankova N., Makarevich S., Kimlenka I., Ivashkevich O. Good real word examples of wood-based sustainable chemistry. *Sustainable Chem. and Pharm.*, 2017, vol. 5, pp. 1–13. doi: 10.1016/j.scp.2016.11.001
 62. Savitskaya T. A., Grinshpan D. D., Tsygankova N. G., Nevar T. N., Gonchar A. N., Reznikov I. V., Telysheva G. M., Arzhanitsa A. S., Dizhbite T. N. Kompozitnoye biotoplivo i udobreniya na osnove gidroliznogo lignin [Composite biofuels and fertilizers based on hydrolytic lignin]. Available at: <http://old.bntu.by/images/stories/News/Forum/Latvia2013/21.pdf> (accessed 02.10.2020).
 63. Savitskaya T. A., Tsygankova N. G., Makarevich S. E., Grinshpan D. D. «Zelenaya» khimiya v novykh tekhnologiyakh pererabotki tsellyulozy i lignina ["Green" chemistry in new technologies for processing cellulose and lignin]. *Materialy dokl. Mezhdunar. nauch.-tekh. konf. «Khimiya i khimicheskaya tekhnologiya pererabotki rastitel'nogo syr'ya»* [Materials of International sci.-tech. conf. "Chemistry and chemical technology of processing plant raw materials"]. Minsk, 2018, pp. 15–19.