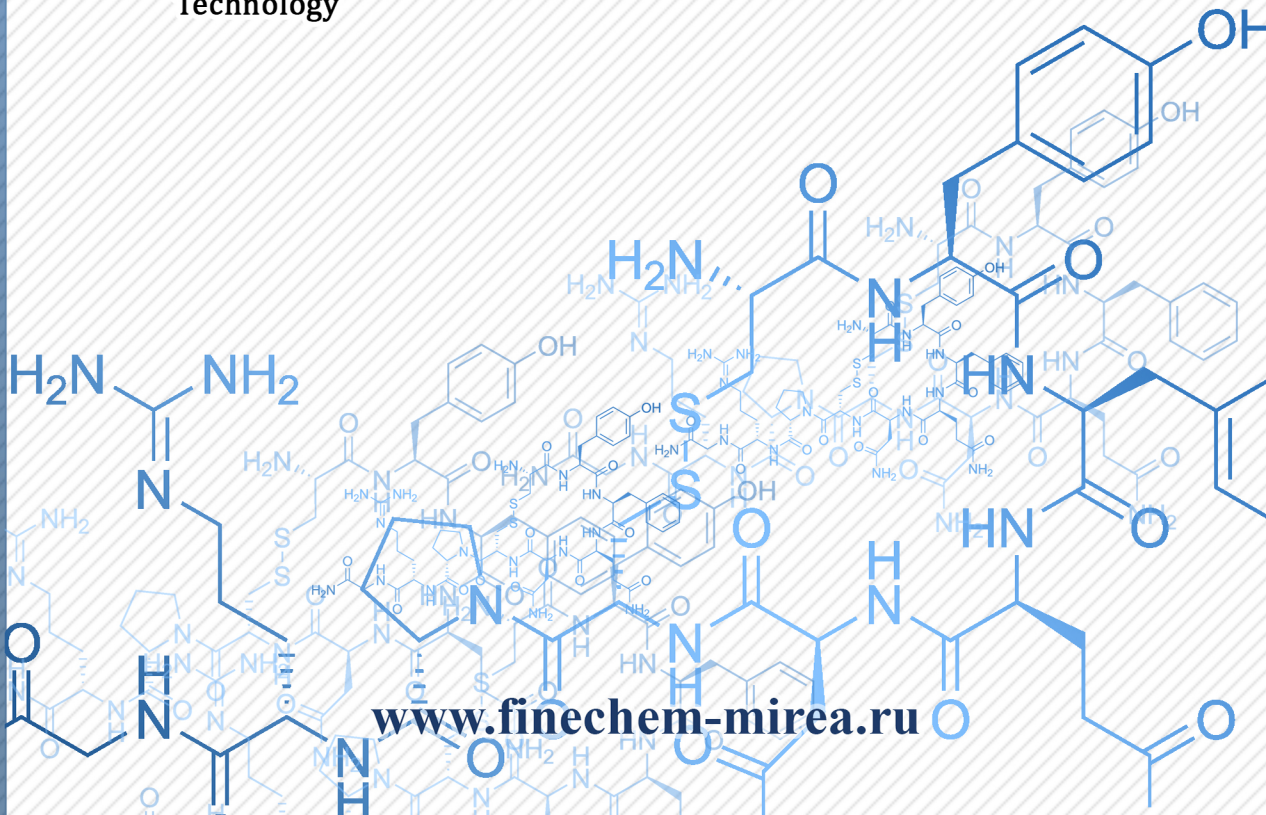
ISSN 2686-7575 (Online)

ТОНКИЕ ХИМИЧЕСКИЕ ТЕХНОЛОГИИ

Fine Chemical Technologies

- Theoretical Bases of Chemical Technology
- Chemistry and Technology of Organic Substances
- Chemistry and Technology of Medicinal Compounds and Biologically Active Substances
- Biochemistry and Biotechnology
- Synthesis and Processing of Polymers and Polymeric Composites
- Chemistry and Technology of Inorganic Materials
- Analytical Methods in Chemistry and Chemical Technology
- Mathematical Methods and Information Systems in Chemical Technology



19(6)
2024

www.finechem-mirea.ru

ISSN 2686-7575 (Online)

ТОНКИЕ ХИМИЧЕСКИЕ ТЕХНОЛОГИИ

Fine Chemical Technologies

- Theoretical Bases of Chemical Technology
- Chemistry and Technology of Organic Substances
- Chemistry and Technology of Medicinal Compounds and Biologically Active Substances
- Biochemistry and Biotechnology
- Synthesis and Processing of Polymers and Polymeric Composites
- Chemistry and Technology of Inorganic Materials
- Analytical Methods in Chemistry and Chemical Technology
- Mathematical Methods and Information Systems in Chemical Technology

Tonkie Khimicheskie Tekhnologii = Fine Chemical Technologies.
Vol. 19, No. 6, 2024

Тонкие химические технологии = Fine Chemical Technologies.
Том 19, № 6, 2024

https://doi.org/10.32362/2410-6593-2024-19-6
www.finechem-mirea.ru

**Tonkie Khimicheskie Tekhnologii =
Fine Chemical Technologies
2024, Vol. 19, No. 6**

The peer-reviewed scientific and technical journal Fine Chemical Technologies highlights the modern achievements of fundamental and applied research in the field of fine chemical technologies, including theoretical bases of chemical technology, chemistry and technology of medicinal compounds and biologically active substances, organic substances and inorganic materials, biochemistry and biotechnology, synthesis and processing of polymers and polymeric composites, analytical and mathematical methods and information systems in chemistry and chemical technology.

Founder and Publisher

Federal State Budget
Educational Institution of Higher Education
"MIREA – Russian Technological University"
78, Vernadskogo pr., Moscow, 119454, Russian Federation.
Publication frequency: bimonthly.
The journal was founded in 2006. The name was Vestnik MITHT until 2015 (ISSN 1819-1487).

The journal is included into the List of peer-reviewed science press of the State Commission for Academic Degrees and Titles of the Russian Federation.

The journal is indexed: SCOPUS, DOAJ, Chemical Abstracts, Science Index, RSCI, Ulrich's International Periodicals Directory

Editor-in-Chief:
Andrey V. Timoshenko – Dr. Sci. (Eng.), Cand. Sci. (Chem.), Professor, MIREA – Russian Technological University, Moscow, Russian Federation. Scopus Author ID 56576076700, ResearcherID Y-8709-2018, https://orcid.org/0000-0002-6511-7440, *timoshenko@mirea.ru*

Deputy Editor-in-Chief:
Valery V. Fomichev – Dr. Sci. (Chem.), Professor, MIREA – Russian Technological University, Moscow, Russian Federation. Scopus Author ID 57196028937, http://orcid.org/0000-0003-4840-0655, *fomichev@mirea.ru*

Executive Editor:
Sergey A. Durakov – Cand. Sci. (Chem.), Associate Professor, MIREA – Russian Technological University, Moscow, Russian Federation, Scopus Author ID 57194217518, ResearcherID AAS-6578-2020, http://orcid.org/0000-0003-4842-3283, *durakov@mirea.ru*

Editorial staff:

Managing Editor	Cand. Sci. (Eng.) Galina D. Seredina
Editor	Sofya M. Mazina
Science editors	Dr. Sci. (Chem.), Prof. Tatyana M. Buslaeva
	Dr. Sci. (Chem.), Prof. Anatolii A. Ischenko
	Dr. Sci. (Eng.), Prof. Anatolii V. Markov
	Dr. Sci. (Chem.), Prof. Vladimir A. Tverskoy
Desktop publishing	Sergey V. Trofimov

86, Vernadskogo pr., Moscow, 119571, Russian Federation.
Phone: +7 (499) 600-80-80 (#31288)
E-mail: *seredina@mirea.ru*

The registration number ПИ № ФС 77-74580 was issued in December 14, 2018 by the Federal Service for Supervision of Communications, Information Technology, and Mass Media of Russia

The subscription index of *Pressa Rossii*: **36924**

**Тонкие химические технологии =
Fine Chemical Technologies
2024, том 19, № 6**

Научно-технический рецензируемый журнал «Тонкие химические технологии» освещает современные достижения фундаментальных и прикладных исследований в области тонких химических технологий, включая теоретические основы химической технологии, химию и технологию лекарственных препаратов и биологически активных соединений, органических веществ и неорганических материалов, биохимию и биотехнологию, синтез и переработку полимеров и композитов на их основе, аналитические и математические методы и информационные системы в химии и химической технологии.

Учредитель и издатель

федеральное государственное бюджетное
образовательное учреждение высшего образования
«МИРЭА – Российский технологический университет»
119454, РФ, Москва, пр-т Вернадского, д. 78.
Периодичность: один раз в два месяца.
Журнал основан в 2006 году. До 2015 года издавался под названием «Вестник МИТХТ» (ISSN 1819-1487).

Журнал входит в Перечень ведущих рецензируемых научных журналов ВАК РФ.

Индексируется: SCOPUS, DOAJ, Chemical Abstracts, РИНЦ (Science Index), RSCI, Ulrich's International Periodicals Directory

Главный редактор:
Тимошенко Андрей Всеволодович – д.т.н., к.х.н., профессор, МИРЭА – Российский технологический университет, Москва, Российская Федерация. Scopus Author ID 56576076700, ResearcherID Y-8709-2018, https://orcid.org/0000-0002-6511-7440, *timoshenko@mirea.ru*

Заместитель главного редактора:
Фомичёв Валерий Вячеславович – д.х.н., профессор, МИРЭА – Российский технологический университет, Москва, Российская Федерация. Scopus Author ID 57196028937, http://orcid.org/0000-0003-4840-0655, *fomichev@mirea.ru*

Выпускающий редактор:
Дураков Сергей Алексеевич – к.х.н., доцент, МИРЭА – Российский технологический университет, Москва, Российская Федерация, Scopus Author ID 57194217518, ResearcherID AAS-6578-2020, http://orcid.org/0000-0003-4842-3283, *durakov@mirea.ru*

Редакция:

Зав. редакцией	к.т.н. Г.Д. Середина
Редактор	С.М. Мазина
Научные редакторы	д.х.н., проф. Т.М. Буслаева
	д.х.н., проф. А.А. Ищенко
	д.т.н., проф. А.В. Марков
	д.х.н., проф. В.А. Тверской
Компьютерная верстка	С.В. Трофимов

РФ, 119571, Москва, пр. Вернадского, 86, оф. Р-108.
Тел.: +7 (499) 600-80-80 (#31288)
E-mail: *seredina@mirea.ru*

Регистрационный номер и дата принятия решения о регистрации СМИ: ПИ № ФС 77-74580 от 14.12.2018 г. СМИ зарегистрировано Федеральной службой по надзору в сфере связи, информационных технологий и массовых коммуникаций (Роскомнадзор)

Индекс по Объединенному каталогу «Пресса России»: **36924**

© MIREA – Russian Technological University, 2024

EDITORIAL BOARD

Andrey V. Blokhin – Dr. Sci. (Chem.), Professor, Belarusian State University, Minsk, Belarus.
Scopus Author ID 7101971167, ResearcherID AAF-8122-2019, https://orcid.org/0000-0003-4778-5872, *blokhin@bsu.by.*

Sergey P. Verevkin – Dr. Sci. (Eng.), Professor, University of Rostock, Rostock, Germany.
Scopus Author ID 7006607848, ResearcherID G-3243-2011, https://orcid.org/0000-0002-0957-5594, *Sergey.verevkin@uni-rostock.de.*

Konstantin Yu. Zhizhin – Corresponding Member of the Russian Academy of Sciences (RAS), Dr. Sci. (Chem.), Professor, N.S. Kurnakov Institute of General and Inorganic Chemistry of the RAS, Moscow, Russian Federation.
Scopus Author ID 6701495620, ResearcherID C-5681-2013, http://orcid.org/0000-0002-4475-124X, *kyuzhizhin@igic.ras.ru.*

Igor V. Ivanov – Dr. Sci. (Chem.), Professor, MIREA – Russian Technological University, Moscow, Russian Federation.
Scopus Author ID 34770109800, ResearcherID I-5606-2016, http://orcid.org/0000-0003-0543-2067, *ivanov_i@mirea.ru.*

Carlos A. Cardona – PhD (Eng.), Professor, National University of Columbia, Manizales, Colombia.
Scopus Author ID 7004278560, http://orcid.org/0000-0002-0237-2313, *ccardonaal@unal.edu.co.*

Elvira T. Krut'ko – Dr. Sci. (Eng.), Professor, Belarusian State Technological University, Minsk, Belarus.
Scopus Author ID 6602297257, *ela_krutko@mail.ru.*

Anatolii I. Miroshnikov – Academician at the RAS, Dr. Sci. (Chem.), Professor, M.M. Shemyakin and Yu.A. Ovchinnikov Institute of Bioorganic Chemistry of the RAS, Member of the Presidium of the RAS, Chairman of the Presidium of the RAS Pushchino Research Center, Moscow, Russian Federation.
Scopus Author ID 7006592304, ResearcherID G-5017-2017, *aiv@ibch.ru.*

Aziz M. Muzafarov – Academician at the RAS, Dr. Sci. (Chem.), Professor, A.N. Nesmeyanov Institute of Organoelement Compounds of the RAS, Moscow, Russian Federation.
Scopus Author ID 7004472780, ResearcherID G-1644-2011, https://orcid.org/0000-0002-3050-3253, *aziz@ineos.ac.ru.*

РЕДАКЦИОННАЯ КОЛЛЕГИЯ

Блохин Андрей Викторович – д.х.н., профессор Белорусского государственного университета, Минск, Беларусь.
Scopus Author ID 7101971167, ResearcherID AAF-8122-2019, https://orcid.org/0000-0003-4778-5872, *blokhin@bsu.by.*

Верёвкин Сергей Петрович – д.т.н., профессор Университета г. Росток, Росток, Германия.
Scopus Author ID 7006607848, ResearcherID G-3243-2011, https://orcid.org/0000-0002-0957-5594, *Sergey.verevkin@uni-rostock.de.*

Жижин Константин Юрьевич – член-корр. Российской академии наук (РАН), д.х.н., профессор, Институт общей и неорганической химии им. Н.С. Курнакова РАН, Москва, Российская Федерация.
Scopus Author ID 6701495620, ResearcherID C-5681-2013, http://orcid.org/0000-0002-4475-124X, *kyuzhizhin@igic.ras.ru.*

Иванов Игорь Владимирович – д.х.н., профессор, МИРЭА – Российский технологический университет, Москва, Российская Федерация.
Scopus Author ID 34770109800, ResearcherID I-5606-2016, http://orcid.org/0000-0003-0543-2067, *ivanov_i@mirea.ru.*

Кардона Карлос Ариэль – PhD, профессор Национального университета Колумбии, Манизалес, Колумбия.
Scopus Author ID 7004278560, http://orcid.org/0000-0002-0237-2313, *ccardonaal@unal.edu.co.*

Крутько Эльвира Тихоновна – д.т.н., профессор Белорусского государственного технологического университета, Минск, Беларусь.
Scopus Author ID 6602297257, *ela_krutko@mail.ru.*

Мирошников Анатолий Иванович – академик РАН, д.х.н., профессор, Институт биоорганической химии им. академиков М.М. Шемякина и Ю.А. Овчинникова РАН, член Президиума РАН, председатель Президиума Пущинского научного центра РАН, Москва, Российская Федерация.
Scopus Author ID 7006592304, ResearcherID G-5017-2017, *aiv@ibch.ru.*

Музафаров Азиз Мансурович – академик РАН, д.х.н., профессор, Институт элементоорганических соединений им. А.Н. Несмеянова РАН, Москва, Российская Федерация.
Scopus Author ID 7004472780, ResearcherID G-1644-2011, https://orcid.org/0000-0002-3050-3253, *aziz@ineos.ac.ru.*

Ivan A. Novakov – Academician at the RAS, Dr. Sci. (Chem.), Professor, President of the Volgograd State Technical University, Volgograd, Russian Federation.
Scopus Author ID 7003436556, ResearcherID I-4668-2015, http://orcid.org/0000-0002-0980-6591, *president@vstu.ru.*

Alexander N. Ozerin – Corresponding Member of the RAS, Dr. Sci. (Chem.), Professor, Enikolopov Institute of Synthetic Polymeric Materials of the RAS, Moscow, Russian Federation.
Scopus Author ID 7006188944, ResearcherID J-1866-2018, https://orcid.org/0000-0001-7505-6090, *ozerin@ispm.ru.*

Tapani A. Pakkanen – PhD, Professor, Department of Chemistry, University of Eastern Finland, Joensuu, Finland.
Scopus Author ID 7102310323, *tapani.pakkanen@uef.fi.*

Armando J.L. Pombeiro – Academician at the Academy of Sciences of Lisbon, PhD, Professor, President of the Center for Structural Chemistry of the Higher Technical Institute of the University of Lisbon, Lisbon, Portugal.
Scopus Author ID 7006067269, ResearcherID I-5945-2012, https://orcid.org/0000-0001-8323-888X, *pombeiro@ist.utl.pt.*

Dmitrii V. Pyshnyi – Corresponding Member of the RAS, Dr. Sci. (Chem.), Professor, Institute of Chemical Biologyand Fundamental Medicine, Siberian Branch of the RAS, Novosibirsk, Russian Federation.
Scopus Author ID 7006677629, ResearcherID F-4729-2013, https://orcid.org/0000-0002-2587-3719, *pyshnyi@niboch.nsc.ru.*

Alexander S. Sigov – Academician at the RAS, Dr. Sci. (Phys. and Math.), Professor, President of MIREA – Russian Technological University, Moscow, Russian Federation.
Scopus Author ID 35557510600, ResearcherID L-4103-2017, *sigov@mirea.ru.*

Alexander M. Toikka – Dr. Sci. (Chem.), Professor, Institute of Chemistry, Saint Petersburg State University, St. Petersburg, Russian Federation.
Scopus Author ID 6603464176, ResearcherI D A-5698-2010, http://orcid.org/0000-0002-1863-5528, *a.toikka@spbu.ru.*

Andrzej W. Trochimczuk – Dr. Sci. (Chem.), Professor, Faculty of Chemistry, Wrocław University of Science and Technology, Wrocław, Poland.
Scopus Author ID 7003604847, *andrzej.trochimczuk@pwr.edu.pl.*

Aslan Yu. Tsivadze – Academician at the RAS, Dr. Sci. (Chem.), Professor, A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of the RAS, Moscow, Russian Federation.
Scopus Author ID 7004245066, ResearcherID G-7422-2014, *tsiv@phyche.ac.ru.*

Новаков Иван Александрович – академик РАН, д.х.н., профессор, президент Волгоградского государственного технического университета, Волгоград, Российская Федерация.
Scopus Author ID 7003436556, ResearcherID I-4668-2015, http://orcid.org/0000-0002-0980-6591, *president@vstu.ru.*

Озерин Александр Никифорович – член-корр. РАН, д.х.н., профессор, Институт синтетических полимерных материалов им. Н.С. Ениколопова РАН, Москва, Российская Федерация.
Scopus Author ID 7006188944, ResearcherID J-1866-2018, https://orcid.org/0000-0001-7505-6090, *ozerin@ispm.ru.*

Пакканен Тапани – PhD, профессор, Департамент химии, Университет Восточной Финляндии, Йоенсуу, Финляндия.
Scopus Author ID 7102310323, *tapani.pakkanen@uef.fi.*

Помбейро Армандо – академик Академии наук Лиссабона, PhD, профессор, президент Центра структурной химии Высшего технического института Университета Лиссабона, Португалия.
Scopus Author ID 7006067269, ResearcherID I-5945-2012, https://orcid.org/0000-0001-8323-888X, *pombeiro@ist.utl.pt.*

Пышный Дмитрий Владимирович – член-корр. РАН, д.х.н., профессор, Институт химической биологии и фундаментальной медицины Сибирского отделения РАН, Новосибирск, Российская Федерация.
Scopus Author ID 7006677629, ResearcherID F-4729-2013, https://orcid.org/0000-0002-2587-3719, *pyshnyi@niboch.nsc.ru.*

Сигов Александр Сергеевич – академик РАН, д.ф.-м.н., профессор, президент МИРЭА – Российского технологического университета, Москва, Российская Федерация.
Scopus Author ID 35557510600, ResearcherID L-4103-2017, *sigov@mirea.ru.*

Тойкка Александр Матвеевич – д.х.н., профессор, Институт химии, Санкт-Петербургский государственный университет, Санкт-Петербург, Российская Федерация.
Scopus Author ID 6603464176, Researcher ID A-5698-2010, http://orcid.org/0000-0002-1863-5528, *a.toikka@spbu.ru.*

Трохимчук Анджей – д.х.н., профессор, Химический факультет Вроцлавского политехнического университета, Вроцлав, Польша.
Scopus Author ID 7003604847, *andrzej.trochimczuk@pwr.edu.pl.*

Цивадзе Аслан Юсупович – академик РАН, д.х.н., профессор, Институт физической химии и электрохимии им. А.Н. Фрумкина РАН, Москва, Российская Федерация.
Scopus Author ID 7004245066, ResearcherID G-7422-2014, *tsiv@phyche.ac.ru.*

19(6) 2024 | Tonkie Khimicheskie Tekhnologii
Fine Chemical Technologies

Contents

СОДЕРЖАНИЕ

Tonkie Khimicheskie Tekhnologii = Fine Chemical Technologies.
2024;19(6):485–496
ISSN 2686-7575 (Online)

UDC 519.87[665.761/532.13+661.666.4]*
https://doi.org/10.32362/2410-6593-2024-19-6-485-496
EDN JTDOHN

CC BY

RESEARCH ARTICLE

A mathematical model of the dynamic viscosity dependence of motor oils on temperature, soot concentration, and its morphology

Anatoly V. Lesin[1], ✉, Alexander V. Isaev[1], Boris P. Tonkonogov[2], Sergey V. Dunaev[1], Albert B. Kulikov[1]

[1] *A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 119991 Russia*

[2] *Gubkin University, Moscow, 119991 Russia*

✉ *Corresponding author, e-mail: lesinav@ips.ac.ru*

Abstract

Objectives. A quick cold start of emergency and auxiliary power units based on diesel engines should be possible at any time without problems and in the shortest possible time. The condition of the engine oil is one of the most important factors influencing the smooth start-up of power plants. During diesel engine operation, engine oil accumulates soot in its composition, negatively affecting its rheological properties. The aim of this research is to develop a mathematical model to describe changes in the dynamic viscosity of motor oils as a function of temperature. This model will account for the concentration of soot and its morphology, based on the results of experimental studies.

Methods. Standardly used motor oils for diesel engines M-14D_2SE and M-5z/14D_2SE were used as oil samples in the preparation of model mixtures. The dispersed phase of the suspensions comprised carbon black of the N110, N220, N330, and N220 grades, characterized by a dusty (nongranular) texture. The rheological properties of the samples were determined using a TA Instruments DHR-2 rotational rheometer. The experimental data was subjected to mathematical statistical processing, in order to obtain approximating dependencies.

Results. The paper presents an analysis of the various approaches to the description of the rheology of suspensions and the results of experimental studies of the viscosity-temperature characteristics (VTCs) of model samples of oils containing soot. The extant models of the dependence of the dynamic viscosity of suspensions on temperature, volume concentration of the dispersed phase, particle size and shape are demonstrated to be inadequate for the description of the VTCs of motor oils containing soot. A model of the rheological properties of soot-oil suspensions is proposed in the form of a mathematical dependence of their dynamic viscosity on temperature, mass concentration of soot, material density and size of soot particles, characteristics of the shape and structure of primary aggregates and the ratio of the sizes of aggregates and molecules of the dispersion medium.

Conclusions. It was demonstrated that a comprehensive description of the VTCs of engine oils containing soot necessitates the consideration of the structural characteristics of the primary aggregates of soot particles. A mathematical model of the VTCs of oils was developed. This model is based on the dependence of the dynamic viscosity of oils on temperature, mass concentration of soot, density of the particle material, degree of non-sphericity of aggregates, the ratio of the particle sizes of the dispersed phase (either aggregates or single particles of non-aggregated soot) and oil molecules, and on the structure of soot, characterized by adsorption of dibutyl phthalate.

Keywords

mathematical model, dynamic viscosity, engine oil, soot, structure of aggregates, rheological properties

Submitted: 20.08.2024
Revised: 16.09.2024
Accepted: 21.10.2024

© A.V. Lesin, A.V. Isaev, B.P. Tonkonogov, S.V. Dunaev, A.B. Kulikov, 2024

For citation

Lesin A.V., Isaev A.V., Tonkonogov B.P., Dunaev S.V., Kulikov A.B. A mathematical model of the dynamic viscosity dependence of motor oils on temperature, soot concentration, and its morphology. *Tonk. Khim. Tekhnol. = Fine Chem. Technol*. 2024;19(6):485–496. https://doi.org/10.32362/2410-6593-2024-19-5-462-478

НАУЧНАЯ СТАТЬЯ

Математическая модель зависимости динамической вязкости моторных масел от температуры, концентрации сажи и ее морфологии

А.В. Лесин[1], ✉, А.В. Исаев[1], Б.П. Тонконогов[2], С.В. Дунаев[1], А.Б. Куликов[1]

[1] *Институт нефтехимического синтеза им. А.В. Топчиева, Российская академия наук, Москва, 119991 Россия*

[2] *Российский государственный университет нефти и газа (национальный исследовательский университет) им. И.М. Губкина, Москва, 119991 Россия*

✉ *Автор для переписки, e-mail: lesinav@ips.ac.ru*

Аннотация

Цели. Быстрый холодный пуск аварийных и вспомогательных энергетических установок на базе дизельных двигателей в любое время должен осуществляться без особых проблем и в кратчайшие сроки. Одним из основных факторов, влияющих на безаварийный пуск энергетических установок, является состояние моторного масла. В процессе работы дизельного двигателя моторное масло накапливает в своем составе сажу, что негативно влияет на его реологические свойства. Цель работы — разработка математической модели изменения динамической вязкости моторных масел в зависимости от температуры с учетом концентрации сажи и ее морфологии на основе результатов экспериментальных исследований.

Методы. В качестве образцов масел для приготовления модельных смесей использовались штатно применяемые моторные масла для дизельных двигателей М-14$Д_2$СЕ и М-5з/14$Д_2$СЕ. В качестве дисперсной фазы суспензий использовался технический углерод марок N110, N220, N330 и N220 пылящий (негранулированный). Реологические свойства образцов определялись на ротационном реометре TA Instruments DHR-2. Полученные экспериментальные данные обрабатывались методами математической статистики с получением аппроксимирующих зависимостей.

Результаты. В работе представлены анализ различных подходов к описанию реологии суспензий и результаты экспериментальных исследований вязкостно-температурных характеристик (ВТХ) модельных образцов масел, содержащих сажу. Показано, что существующие модели зависимости динамической вязкости суспензий от температуры, объемной концентрации дисперсной фазы, размеров и формы ее частиц не позволяют адекватно описать ВТХ моторных масел, содержащих сажу. Предложена модель реологических свойств саже-масляных суспензий в виде математической зависимости их динамической вязкости от температуры, массовой концентрации сажи, плотности материала и размеров сажевых частиц, от характеристик формы и структуры первичных агрегатов, а также от соотношения размеров агрегатов и молекул дисперсионной среды.

Выводы. Показано, что для адекватного описания ВТХ моторных масел, содержащих сажу, необходимо учитывать характеристики структуры первичных агрегатов сажевых частиц. Разработана математическая модель ВТХ масел в виде зависимости их динамической вязкости от температуры, массовой концентрации сажи, плотности материала частиц, степени несферичности агрегатов, соотношения размеров частиц дисперсной фазы (агрегатов или одиночных частиц неагрегированной сажи) и молекул масла, а также структурности сажи, характеризуемой стандартным показателем — адсорбцией дибутилфталата.

Ключевые слова

математическая модель, динамическая вязкость, моторное масло, сажа, структура агрегатов, реологические свойства

Поступила: 20.08.2024
Доработана: 16.09.2024
Принята в печать: 21.10.2024

Для цитирования

Лесин А.В., Исаев А.В., Тонконогов Б.П., Дунаев С.В., Куликов А.Б. Математическая модель зависимости динамической вязкости моторных масел от температуры, концентрации сажи и ее морфологии. *Тонкие химические технологии*. 2024;19(6):485–496. https://doi.org/10.32362/2410-6593-2024-19-5-462-478

INTRODUCTION

Among the numerous attributes of motor oil (MO), its viscosity-temperature characteristic (VTC) is of particular significance. The viscosity of the oil is a critical factor in determining the operational characteristics of diesel engines, including the starting properties, time to reach full load acceptance, operational fuel consumption, and energy costs associated with driving its units. The viscosity of the oil affects these characteristics by influencing the friction operation of the engine and the energy required to drive its units. The viscosity of the oil also exerts an influence on the total emissions of toxic substances with exhaust gases, given that the mass of emissions is proportional to fuel consumption, which increases in proportion to the viscosity of the oil, provided that the external load remains constant.

The VTC of MO provides a comprehensive characterization of the rheological properties in question. The VTC of MO is primarily determined by the nature of the base oil. Viscosity-enhancing additives are frequently employed to augment viscosity and viscosity index. The utilization of these compounds facilitates the attainment of oils with a mild VTC. The combination of thickening additives with additives which enhance lubricating properties enables the production of energy-efficient oils [1].

The analysis demonstrates that the viscosity of MO is not a constant during operation and varies in accordance with the accumulation of various contaminants within it. The introduction of engine fuel into the oil results in a reduction in viscosity, while the flash point in the open crucible is also diminished. This is a useful diagnostic parameter for identifying engine malfunctions which may lead to oil liquefaction by engine fuel.

It is typical for a small quantity of wear products to be present in the operational MO. This is due to the formation and removal of such products from the friction zones by the MO. Additionally, the effective removal of these products from the oil stream by cleaning filters, as well as the settling of heavy particles of wear products in the crankcase contribute to the overall reduction in their concentration.

The greatest number of contaminants present within the operational MO, which are perpetually present within the circulating stream, are minute soot particles not retained by the filters. These particles often contain adsorbed products of degradation and chemical transformation of oil components during operation.

The bulletin[1] indicates that the presence of soot in the oil is not problematic until the active components of the additives reach a point of diminishing effectiveness. The accumulation of soot in the crankcase over time leads to the removal of additive components from the surface of the soot. This in turn results in the accelerated wear of the rubbing parts, namely the cylinder piston group and the valve mechanism.

As the concentration of soot in MO increases, its viscosity also increases. This gradual increase reaches a point at which the operation of the diesel engine becomes impossible. At this point, the oil is replaced with fresh oil. Concurrently, augmentation in the viscosity of the oil due to accumulation of soot may be obscured by a reduction in viscosity resulting from the introduction of fuel into the oil.

Given the labor-intensive and economically unprofitable nature of constant monitoring of the condition of the working oil, there is a clear interest in developing a mathematical model for changing the dynamic viscosity of MO in accordance with the increasing concentration of soot during engine operation.

MATERIALS AND METHODS

Materials

To study the rheological properties of suspensions, M-14D_2SE and M-5z/D_2SE oils, routinely used in medium-speed diesel engines (*Shahumyan Production Plant*, Russia), were selected.

The trademarks of carbon black N110, N220, N220p (dusty, selected from the bag filter of the installation before granulation), and N330 of production by *Nizhnekamsktehuglerod* (Russia) were used as the dispersed phase in the research.

In the interests of reducing the volume of the article, the results of experiments for MO of M-14D_2SE and N220p grades, as a dispersed phase, will be further considered.

The approximation for the dependence of pure oil is given by the following equation:

$$\mu(T) = \exp\left(\exp\left(a \cdot T^{-4} + b \cdot T^{-2} + c\right)\right) - 1. \quad (1)$$

The values of the coefficients in Eq. (1) are: $a = -1.29 \cdot 10^{10}$; $b = 1.03 \cdot 10^{6}$; $c = -1.13$.

Methods

The rheological properties of the model samples were investigated utilizing a rotational rheometer (DHR-2, *TA Instruments*, USA) with a cone-plane measuring unit

[1] Cummins service Bulletin 4960819-07. 2002. 15 p.

(plane diameter 40 mm, cone angle 2°). The temperature dependencies of viscosity were obtained at a constant shear rate of 100 c^{-1} and a temperature change rate of 2°C/min with an increase in temperature from 20 to 120°C and with a decrease in temperature from room temperature to −60°C.

Analysis of analytical approaches to the description of VTC soot-oil suspensions

The majority of the dependencies proposed in scientific and technical literature with regard to the dynamic viscosity of dispersed systems can be reduced to the following form:

$$\mu(T,\varphi) = \mu_0(T) \cdot F(\varphi), \quad (2)$$

wherein $\mu_0(T)$ is the dynamic viscosity of the dispersion medium as a function of absolute temperature; $F(\varphi)$ is a function of the volume concentration of the dispersed phase.

One of the first known formulas for calculating the viscosity of suspensions was proposed by A. Einstein [2]:

$$\mu(\varphi) = \mu_0 \cdot F(\varphi) = \mu_0 \cdot (1 + \varepsilon \cdot \varphi), \quad (3)$$

wherein ε is the coefficient for particles of the dispersed phase of an ellipsoid shape (in particular, for spherical particles in the formula theoretically derived by Einstein, with the assumptions he made when calculating energy dissipation when a viscous liquid flows around a solitary sphere, the value ε is 2.5, and the experimentally obtained value ε for spherical particles is 2.9); μ_0 is viscosity at a fixed temperature.

It can be observed that Eq. (3) represents a special case of Eq. (2). Consequently, the viscosity of the suspension is dependent on temperature solely in relation to the viscosity of the dispersion medium. It should be noted that the dependence of the form (3) produces correct results only at $\varphi < 0.04$, when the hydrodynamic interaction between the particles of the dispersed phase can be neglected.

At elevated concentrations of dispersed phase particles in suspensions, the interaction of the flow fields of the dispersion medium around neighboring particles becomes discernible. The viscosity exhibits a nonlinear increase as the concentration of the dispersed phase rises. In this instance, a more comprehensive equation is more appropriate [2]:

$$\mu(\varphi) = \mu_0 \cdot \left(1 + \varepsilon_1 \cdot \varphi + \varepsilon_2 \cdot \varphi^2 + \varepsilon_3 \cdot \varphi^3\right), \quad (4)$$

wherein the values of the coefficients ε_1, ε_2, ε_3 are different for different authors. In [3], numerous variants of the values of these coefficients for different ranges of values are given, while in almost all literary sources $\varepsilon_1 = 2.5$, and the remaining coefficients may differ significantly. For example, in [4] the Wand formula with the coefficients $\varepsilon_1 = 2.5$, $\varepsilon_2 = 6.25$, $\varepsilon_3 = 15.6$ is given. They allow a sufficiently high accuracy of calculation of viscosity of suspensions to be obtained with a low content of dispersed phase ($\varphi < 0.3$), when collisions of particles and overlapping of solvate layers formed by a part of the dispersion medium are so rare that their influence on the flow of suspensions is very insignificant.

Formulas are proposed for calculating the viscosity of suspensions in which the volume concentration function of the dispersed phase $F(\varphi)$ has a different form. Thus, in the fundamental monograph by S. Bretschneider [3], the Kunitz formula is given:

$$\mu(\varphi) = \mu_0 \cdot (1 + 0.5 \cdot \varphi) \cdot (1 - \varphi)^4, \quad (5)$$

However, calculations based on these formulas produce absolutely incorrect and contradictory results to experimental data. This is obviously due to an error in the "–" sign in the second bracket. It is regrettable that this error has been identified in numerous other reviews and reference publications.

Upon replacing the "–" sign with "+", the outcomes of the calculations conducted in accordance with Eq. (5) are observed to be relatively proximate to those derived from other validated approximations.

Kurgaev's formula is also given in [3], which, according to the author [3], gives the best agreement with the results of experimental determination of the dynamic viscosity of suspensions in the range of values $\varphi < 0.25$:

$$\mu(\varphi) = \mu_0 \cdot \left(1 + \frac{2 \cdot \varphi}{\left(1 - 1.2 \cdot \varphi^{\frac{2}{3}}\right)^2}\right). \quad (6)$$

The formula for concentrated suspensions exhibiting non-Newtonian properties, as proposed by Barney and Mirzakhi, is presented in reference [4].

$$\mu(\varphi) = \mu_0 \cdot \exp\left(\frac{k_1 \cdot \varphi}{1 - k_2 \cdot \varphi}\right), \quad (7)$$

wherein $k_1 = 2.5$; $k_2 = 0.75$ ... 1.5 for different authors.

The approximations (3)–(7) discussed above do not take into account the size and shape of the particles, despite the necessity of such considerations for certain ratios of concentration and particle sizes of the dispersed phase. In this regard, the following approximation is proposed in reference to suspensions comprising spherical particles, as documented in [4].

$$\mu(\varphi) = \mu_0 \cdot \left(1 + 2.5 \cdot \varphi + \frac{3}{4} \cdot \varphi \cdot \exp\left(\frac{m \cdot \varphi}{(\varphi - \varphi_{max})^2}\right)\right), \quad (8)$$

wherein m = 2.2 + 0.033a; a is the particle size in microns; φ_{max} = 0.74 is the concentration of particles with the densest packaging.

G.I. Kelbaliev [4] notes that the results of calculating the viscosity of suspensions by Eq. (8) agree well with the experimental data. However, like the authors of several other works (e.g., M.A. Morozova[2] and P.I. Pilov [5]), he makes an erroneous conclusion that viscosity also increases with increasing particle size of the dispersed phase.

In the work of P.I. Pilov [5], a theoretically justified formula was proposed for calculating the dynamic viscosity coefficient of suspensions. His formula takes into account not only the volume concentration of the dispersed phase φ and the radius of its particles r, but also the properties of their surface by introducing into the formula the thickness of the boundary layer of the dispersion medium on the surface of the particles of the dispersed phase λ:

$$\mu(\varphi, r, \lambda) = \mu_0 \cdot \frac{1}{1 - \left(1 + \frac{\lambda}{r}\right) \cdot \sqrt[3]{\frac{\varphi}{k_v}}}, \quad (9)$$

wherein k_v is the packing coefficient of particles of the dispersed phase, equal to π/6 for cubic packaging and 0.625 for arbitrary packaging.

As illustrated by Eq. (9), a reduction in the particle size of the dispersed phase is associated with an increase in suspension viscosity. It should be noted that the work [5] is primarily concerned with the gravitational separation of minerals, and therefore pertains mainly to coarse-dispersed suspensions. Therefore, the adequacy of this formula in relation to soot suspensions in MO requires verification.

The work of V.Ya. Rudyak [6], devoted to the study of the viscosity of nanofluids (that is to say, dispersed systems consisting of liquid and nanoparticles, which include non-aggregated carbon black in MO), demonstrated that the dependence of the viscosity of the suspension on the concentration of nanoparticles, regardless of the particle material, can be described by the formula:

$$\mu(\varphi) = \mu_0 \cdot \left(1 + \varepsilon_1 \cdot \varphi + \varepsilon_2 \cdot \varphi^2\right), \quad (10)$$

in which the coefficients ε_1 and ε_2 significantly exceed in magnitude the similar coefficients in Eq. (4).

Thus, in the dependencies for suspensions with TiO_2 nanoparticles, they are 5.45 and 108.2, respectively, in contrast to 2.5 and 6.25 in Wand's formula [4]. For suspensions of aluminum oxide(III) particles, ε_1 and ε_2 are equal to 7.3 and 123, and for copper particles, they are 3.645 and 468.72, respectively. From this, the author [6] concludes that the viscosity coefficient of nanofluids increases significantly faster with increasing particle concentration than the viscosity coefficient of a conventional dispersed liquid. The values of the coefficients ε_1 and ε_2 may depend on the size of the nanoparticles and their material.

As a result of molecular dynamic modeling [6], a dependence was obtained:

$$\mu(\varphi) = \mu_0 \cdot \left[\mu_{rB} + \left(5.25 \cdot \varphi + 40.94 \cdot \varphi^2\right) \times \exp\left(-0.208 \cdot \frac{D}{d}\right)\right], \quad (11)$$

wherein $\mu_{rB} = 1 + 2.5 \cdot \varphi + 6.2 \cdot \varphi^2$ is the relative viscosity of the suspension in the Batchelor's formula [7], D is the effective diameter of the nanoparticles, d is the effective diameter of the molecules of the dispersion medium. Additionally, as demonstrated in reference [6], the rheological characteristics of non-Newtonian nanofluids can be effectively represented by a model of the following form:

$$\mu(\varphi) = K \cdot \gamma^{n-1}, \quad (12)$$

wherein γ is the shear rate; $n = 1 - 36.3 \cdot \varphi + 5 \cdot \varphi^2$; $K = 0.001 + \varphi - 230 \cdot \varphi^2 + 3700 \cdot \varphi^3$.

The author [6] proposes that the Newtonian behavior of nanofluids can be discussed only when the base liquid is Newtonian and the concentration of nanoparticles is not particularly high. The volume concentrations of nanoparticles in this instance does not appear to exceed 10–15%. The coefficient of dynamic viscosity at such concentrations can be represented by the Eq. (10). Nevertheless, the coefficients in this ratio must be functions of the size of the nanoparticles.

$$\mu(\varphi) = \mu_0 \cdot \left(1 + \varepsilon_1(D) \cdot \varphi + \varepsilon_2(D) \cdot \varphi^2\right). \quad (13)$$

In order to evaluate the suitability of the aforementioned approximations, calculations were conducted to determine the kinematic viscosity of M-14D_2SE oil and soot suspensions based on this oil and carbon black grade N220 (dusty) within a temperature range of 250 to 350 K. The resulting data is presented

[2] Morozova M.A. *Thermal conductivity and viscosity of nanofluids*. Diss. Cand. Sci. (Phys.-Math.). Novosibirsk: Institute of Thermophysics SB RAS; 2019. 103 p. (in Russ.).

in Fig. 1. The N220 brand was chosen since, of the available carbon black trademarks, it is morphologically closest to the soot samples described in publications on the problems of soot formation in diesels [8–14].

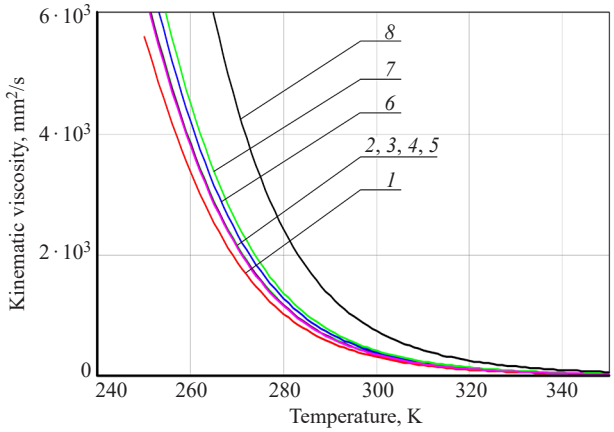


Fig. 1. Approximations for the VTCs of M-14D$_2$SE oil (*1*) and its suspensions with soot (5 vol %) according to the Eqs.: curve (*2*) — Eq. (3); (*3*) — (6); (*4*) — (4); (*5*) — (7); (*6*) — (5); (*7*) — (11); (*8*) — (9)

As can be seen from Fig. 1, all the methods considered for calculating VTCs give a similar nature of dependencies. The majority of formulas which solely consider the volume concentration of the dispersed phase yield highly comparable results for viscosity calculations. Concurrently, the Einstein formula yielded slightly lower viscosity values than the formulas of Kurgaev, Wand, Barney, and Mirzakhi (the latter three yielded almost indistinguishable results).

The VTCs of soot-oil suspensions are also adequately described using the Kunitz model, although it does not account for the particle sizes of the dispersed phase (curve *6* in Fig. 1).

In the context of this study, the model (11) described in the work of V.Ya. Rudyak [6] is the most appropriate when calculating the viscosity of suspensions. This is due to its suitability for a wide range of volume concentrations of the dispersed phase and its consideration of the ratio of particle sizes and molecules of the dispersion medium.

RESULTS AND DISCUSSION

In order to confirm the applicability of the model (11), selected following an analysis of the models available in the scientific and technical literature and a discussion of the same in the previous section, a series of experiments was conducted with the preparation of model mixtures of MO of M-14D$_2$SE grade with different soot contents (N220p dusty, nongranular), followed by the determination of dynamic viscosity. In order to prepare the model samples, soot mass concentrations of 1, 2, 3, 4, 5, and 7 wt % were selected. The 1% step was selected in order to facilitate the observation of the change in viscosity which occurs with an increase in soot concentration. A contamination level of 5 wt % in used oil is typically deemed inadequate, necessitating the replacement of the oil in accordance with the specifications provided by the manufacturers of the associated equipment. The 7 wt % soot content was selected to substantiate the hypothesis that an excess of soot content above the established norm (5 wt %) has a deleterious effect on the rheological characteristics of the oil.

Based on experimental data, approximate dependencies of change of dynamic viscosity of M-14D$_2$SE oil with N220 dusty soot at concentrations of 1, 2, 3, 4, 5, and 7 wt % at absolute temperature were obtained, graphs of which are presented in Fig. 2. The analytical form of the approximating dependencies and the values of the coefficients *a*, *b*, and *c* are presented in Table 1 for reference.

A common feature of the VTCs of M-14D$_2$SE oil samples with soot is the expected steady trend towards an increasingly noticeable shift in viscosity-temperature curves upward relative to the VTC of pure oil as the concentration of soot increases. The highest values of dynamic viscosity can be observed in oil samples with the highest soot content, which in our case corresponds to a concentration of 7 wt %.

Dependence (11) is a suitable method for calculating the dynamic viscosity of suspensions across a wide range of volume concentrations of the dispersed phase and temperatures. In addition to these parameters, it allows for the consideration of only the ratio of the sizes of soot particles and molecules of the dispersion medium (oil). Nevertheless, the outcomes of the calculations indicate that these parameters are inadequate for accurately predicting the VTCs of the oil flow contaminated with soot (Fig. 3).

It is evident that the Eq. (11) does not account for two key factors: firstly, the presence of soot in oil is predominantly in the form of primary aggregates, formed in the gas phase and subsequently captured by oil; and secondly, soot aggregates contain absorbed oil. Given these considerations, the viscosity of soot suspensions in MO must be calculated with a focus on particles of a sufficiently large size, corresponding to the dimensions of soot aggregates. Furthermore, when determining the volume concentration of the dispersed phase, it is essential to take into account the proportion of the dispersion medium which becomes part of the dispersed phase, comparable in volume to the volume of soot.

The average value of the effective particle diameter of the model carbon black (nongranulated carbon black of the N220 brand), designated N220p, considered in this study, is 32 nm, and their primary aggregates are 103 nm [15].

Table 1. Parameters of approximating dependencies of the dynamic viscosity of M-14D$_2$SE oil and suspensions based on it

Product	Dependence coefficients $\mu(T) = \exp\left(\exp\left(a \cdot T^{-4} + b \cdot T^{-2} + c\right)\right) - 1$			Correlation coefficient $\mathrm{corr}\left(\left(T^{-4} + T^{-2}\right), \ln\ln\left(\mu + 1\right)\right)$
	a	*b*	*c*	
M-14D$_2$SE	$-7.31 \cdot 10^9$	$8.60 \cdot 10^5$	−9.84	0.999
M-14D$_2$SE + 1 wt % N220p	$-3.98 \cdot 10^9$	$7.38 \cdot 10^5$	−8.75	0.999
M-14D$_2$SE + 2 wt % N220p	$-3.62 \cdot 10^8$	$6.08 \cdot 10^5$	−7.62	0.999
M-14D$_2$SE + 3 wt % N220p	$2.01 \cdot 10^9$	$5.26 \cdot 10^5$	−6.91	0.999
M-14D$_2$SE + 4 wt % N220p	$5.93 \cdot 10^9$	$3.71 \cdot 10^5$	−5.49	0.999
M-14D$_2$SE + 5 wt % N220p	$9.57 \cdot 10^9$	$2.10 \cdot 10^5$	−3.92	0.998
M-14D^{2}SE + 7 wt % N220p	$-7.31 \cdot 10^9$	$8.60 \cdot 10^5$	−9.84	0.999

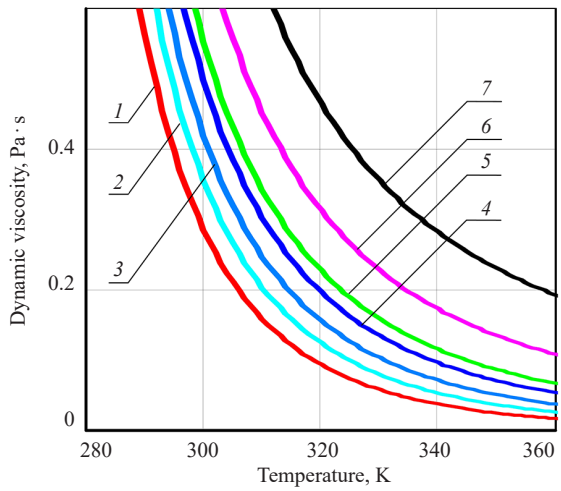


Fig. 2. Approximating dependencies of the dynamic viscosity of M-14D$_2$SE (*1*) oil on temperature at different concentrations of N220 dusty soot:
(*2*) M-14D$_2$SE oil + 1% soot; (*3*) M-14D$_2$SE oil + 2% soot;
(*4*) M-14D$_2$SE oil + 3% soot; (*5*) M-14D$_2$SE oil + 4% soot;
(*6*) M-14D$_2$SE oil + 5% soot; (*7*) M-14D$_2$SE oil + 7% soot

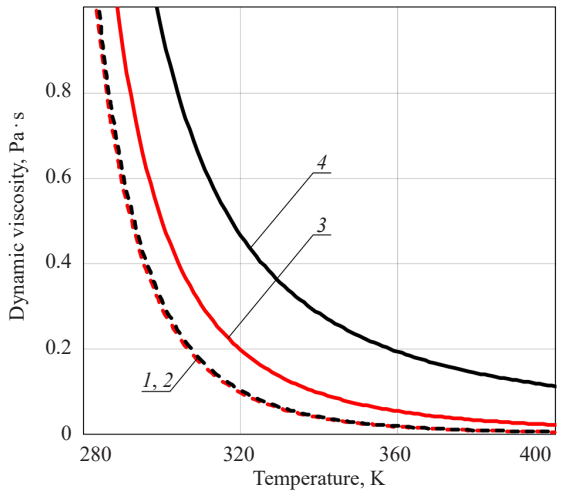


Fig. 3. Results of calculating the dynamic viscosity of 3- and 7-percent suspensions of N220p soot in M-14D$_2$SE engine oil according to Eq. (11) in comparison with the approximation of experimental data:
(*1*) calculation results using Eq. (11) with 3% soot;
(*2*) calculation results using Eq. (11) with 7% soot;
(*3*) M-14D$_2$SE oil + 3% soot; (*4*) M-14D$_2$SE oil + 7% soot

In the absence of consideration of oil absorption by soot aggregates, the dynamic viscosity of soot suspensions in oil, as derived from Eq. (11), exhibits the following dependence:

$$\mu_{s9}(g,T) = \mu_0(T)\left\{\left[1 + 2.5 f_{\mathrm{ns}} c_{\mathrm{DP}}(g,T) + 6.2 f_{\mathrm{ns}}^2 c_{\mathrm{DP}}(g,T)^2\right] + \left[5.25 f_{\mathrm{ns}}^2 c_{\mathrm{DP}}(g,T)^2 + 40.94 f_{\mathrm{ns}}^4 c_{\mathrm{DP}}(g,T)^4\right] \exp\left(-0.208 \frac{D}{d}\right)\right\}, \quad (14)$$

wherein g is the mass concentration of soot in the suspension in fractions of one; T is the absolute temperature, K; $\mu_0(T)$ is the dynamic viscosity of pure oil, Pa · c (general view of the dependence $\mu(T)$ and the values of the coefficients a, b, c are shown in Figs. 1 and 2 and in Table 1, respectively); f_{ns} is the coefficient of non-sphericity of primary aggregates of soot particles, taking into account the ratio of the large and small axes of the space area occupied by the average aggregate; D is the average value of the effective diameter of the aggregates, nm (for N220p soot

according to data [15, 16, [3]] D = 103 nm); d is the characteristic value the linear size of the molecules of the dispersion medium (DM), assumed to be 1.5 nm; $c_{DP}(g,T)$ is the volume concentration of soot in the suspension, calculated by the formula:

$$c_{DP}(g,T)=\frac{g\cdot\rho_{DM}(T)}{g\cdot\rho_{DM}(T)+(1-g)\rho_{DP}}, \quad (15)$$

wherein ρ_{DP} is the density of the dispersed phase material (soot), assumed to be equal to 1850 kg/m^3; $\rho_{DM}(T)$ is the dependence of the density of the DM on temperature:

$$\rho_{DM}(T)=1019-0.661\cdot T. \quad (16)$$

The calculations, performed according to Eq. (14) and presented in Fig. 4, show an unsatisfactory agreement of their results with experimental data obtained using a rotational viscometer.

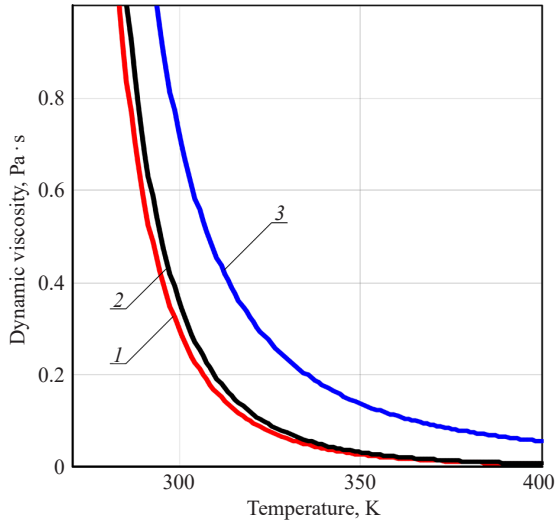


Fig. 4. Results of the calculation of the dynamic viscosity of a 5-percent suspension of N220p soot in M-14D$_2$SE engine oil according to Eq. (14) in comparison with the approximation of experimental data:
(*1*) M-14D$_2$SE oil;
(*2*) calculated value according to Eq. (14);
(*3*) M-14D$_2$SE oil + 5% soot

One of the reasons for this result, clearly, is that Eq. (14) does not take into account the structure of soot, usually characterized by such an indicator as the absorption of dibutyl phthalate k_{DBP}, cm^3/100 g of soot. The value of this indicator is approximately equivalent to the volume of oil absorbed by the primary soot aggregates and subsequently removed from the dispersion medium. This results in an increase in the volume concentration of the dispersed phase in the suspension, with a higher k_{DBP} value leading to a greater degree of separation.

In this case, the volume concentration of the dispersed phase is equal to

$$c_{DP}(g,T,K_{DBP})=\frac{g\cdot\left[1+\rho_{DP}K_{DBP}\right]\rho_{DM}(T)}{g\cdot\rho_{DM}(T)+(1-g)\cdot\rho_{DP}}, \quad (17)$$

wherin $K_{DBP}=k_{DBP}\cdot10^{-5}$, m^3/kg.

Taking into account (17), Eq. (14) takes on a different form:

$$\mu_{s10}(g,T,K_{DBP})=\mu_0(T)\times$$
$$\times\left\{\left[1+2.5f_{ns}c_{DP}(g,T,K_{DBP})+\right.\right.$$
$$\left.+6.2f_{ns}^2c_{DP}(g,T,K_{DBP})^2\right]+ \quad (18)$$
$$+\left[5.25f_{ns}^2c_{DP}(g,T,K_{DBP})^2+\right.$$
$$\left.\left.+40.94f_{ns}^4c_{DP}(g,T,K_{DBP})^4\right]\exp\left(-0.208\frac{D}{d}\right)\right\}.$$

It should be noted that with a mass concentration of soot in a suspension g = 0.05, the volume concentration calculated by Eq. (15) at a temperature of 293 K is 0.023, and according to Eq. (17) in the case of M-14D$_2$SE oil (K_{DBP} = 115 cm^3/100 g) it is 0.072, which causes the larger, than according to Eq. (14), proximity of the obtained viscosity values to those measured experimentally (Fig. 5).

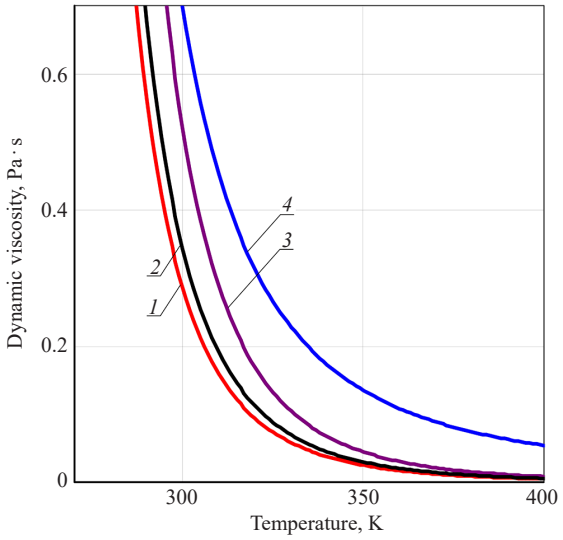


Fig. 5. Results of calculating the dynamic viscosity of a 5-percent suspension of N220p soot in M-14D$_2$SE engine oil according to Eqs. (14) and (18) in comparison with the approximation of experimental data:
(*1*) M-14D$_2$SE oil;
(*2*) calculated value according to Eq. (14);
(*3*) calculated value according to Eq. (18);
(*4*) M-14D$_2$SE oil + 5% soot

[3] Razdiakonova G.I. *Dispersed carbon.* An educational electronic publication of local distribution. Omsk: OmSTU, 2013. 231 p.

Nevertheless, the calculated values of the dynamic viscosity of the oil obtained by Eq. (18) remain significantly disparate from the experimental data. Similar discrepancies were observed for other values of the mass concentration of soot in the suspension, ranging from 0.01 to 0.07.

In light of the aforementioned considerations, an effort was made to incorporate the impact of the shape of primary soot aggregates on the viscosity of suspensions. In the case of N220p, the electron microscopy data presented in [15, 17] indicate that the shape deviates significantly from a spheroidal or ellipsoidal form, exhibiting a branched structure with an average number of soot particles in aggregates equal to 33.

Given that the primary aggregates of N220p soot in size can be classified as Brownian particles, which, due to their branched shape, exhibit a higher resistance to shear motion of the dispersion medium than spherical particles, Eq. (18) was transformed by introducing an additional complex parameter $K(T)$ into it.

$$K\left(T,K_{\text{DBP}}\right)=\left(\frac{K_{\text{DBP}}}{30}\right)\cdot\left(\frac{T}{T_{\text{cr}}}\right)^{0.6}\times \\ \times\left\{\exp\left[-\left(\frac{273}{T}\right)^{3}\right]\right\}^{0.8}, \quad (19)$$

where T_{cr} is the pour point of the oil (for M-14D$_2$SE, T_{cr} = 261 K).

In this instance, the formula for calculating the dynamic viscosity is given by the following expression:

$$\mu_{s11}\left(g,T,K_{\text{DBP}}\right)=\mu_0\left(T\right)\times \\ \times\left\{\left[\left(K\left(T,K_{\text{DBP}}\right)\right)^2\cdot\left(c_{\text{DP}}\left(g,T,K_{\text{DBP}}\right)\right)^{0.3}+\right. \\ 2.5f_{\text{ns}}c_{\text{DP}}\left(g,T,K_{\text{DBP}}\right)+ \\ \left.+\,6.2f_{\text{ns}}^2c_{\text{DP}}\left(g,T,K_{\text{DBP}}\right)^2\right]+ \quad (20) \\ +\left[5.25f_{\text{ns}}^2c_{\text{DP}}\left(g,T,K_{\text{DBP}}\right)^2+\right. \\ \left.\left.+\,40.94f_{\text{ns}}^4c_{\text{DP}}\left(g,T,K_{\text{DBP}}\right)^4\right]\exp\left(-0.208\frac{D}{d}\right)\right\}.$$

The results of the calculation of the dynamic viscosity of oils in accordance with Eq. (20) are shown in Fig. 6.

The relative position of the VTCs of soot suspensions obtained by calculation according to Eq. (20) and the approximate dependencies obtained as a result of processing the experimental data by regression analysis methods indicate a sufficiently high reliability of predicting the viscosity of oils contaminated with soot using Eq. (20).

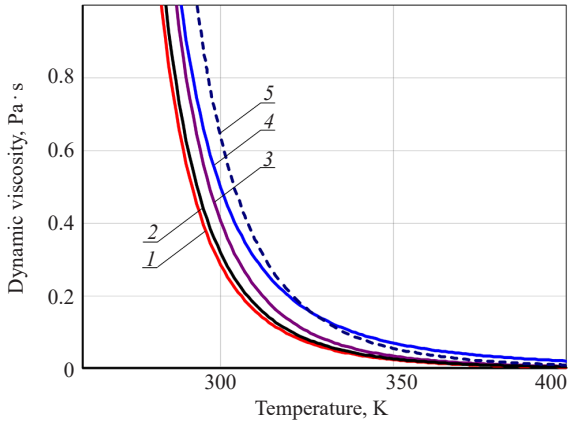


Fig. 6. Results of calculating the dynamic viscosity of a 5-percent suspension of N220p soot in M-14D$_2$SE engine oil according to Eqs. (14), (18), and (20) in comparison with the approximation of experimental data:
(*1*) M-14D$_2$SE oil;
(*2*) calculated value according to Eq. (14);
(*3*) calculated value according to Eq. (18);
(*4*) M-14D$_2$SE oil + 5% soot;
(*5*) calculated value according to Eq. (20)

CONCLUSIONS

The results obtained indicate that, in order to adequately describe the VTCs of MOs containing soot, the characteristics of the structure of the primary aggregates of soot particles need to be taken into account. The developed mathematical model of VTCs of oils in the form of dependence of their dynamic viscosity on temperature, soot mass concentration, density of particles material, degree of aggregates non-sphericity, ratio of particle sizes of dispersed phase (aggregates or single particles of non-aggregated soot) and oil molecules, as well as soot structure characterized by adsorption of dibutyl phthalate, allows the VTCs of oils contaminated with soot formed in the course of diesel operation to be sufficiently reliably predicted.

Authors' contributions

A.V. Lesin—planning and conducting experimental studies, processing test results, preparing the data obtained for publication.

A.V. Isaev—setting objectives, planning the experimental studies, theoretical studies of dispersed phase characteristics effect on the viscosity of suspensions, preparing the data obtained for publication.

B.P. Tonkonogov—setting objectives, processing the data obtained, preparing of the data obtained for publication.

S.V. Dunaev—setting objectives, planning the experimental studies, processing the data obtained, preparing the data obtained for publication.

A.B. Kulikov—setting objectives, planning the experimental studies, processing the data obtained, preparing the data obtained for publication.

The authors declare no conflicts of interest.

REFERENCES

1. Anisimov I.G., *et al. Topliva, smazochnye materialy, tekhnicheskie zhidkosti. Assortiment i primenenie* (*Fuels, Lubricants, Technical Fluids. Assortment and Application*). Shkolnikov V.M. (Ed.). Moscow: Tekhinform; 1999. 596 p. (in Russ.). ISBN 5-89551-006-X
2. Matveenko V.N., Kirsanov E.A. The viscosity and structure of dispersed systems. *Moscow Univ. Chem. Bull*. 2011;66(4): 199–228. https://doi.org/10.3103/S0027131411040079 [Original Russian Text: Matveenko V.N., Kirsanov E.A. The viscosity and structure of dispersed systems. *Vestnik Moskovskogo Universiteta. Khimiya*. 2011;52(4):243–246 (in Russ.).]
3. Bretshnaider S. *Svoistva gazov i zhidkostei. Inzhenernye metody rascheta* (*Properties of Gases and Liquids. Engineering Calculation Methods*). Transl. from Polish. Moscow, Leningrad: Khimiya; 1966. 535 p. (in Russ.). [Bretsznajder S. *Wlasności Gazów i Cieczy*. Warszawa: Wydawnictwa Naukowo-Techniczne; 1962. 739 p.]
4. Kelbaliev G.I., Rasulov R.S., Tagiev D.B. *Mekhanika i reologiya neftyanykh dispersnykh system* (*Mechanics and Rheology of Petroleum Dispersed Systems*). Moscow: Maska; 2017. 462 p. (in Russ.).
5. Pilov P.I. *Gravitatsionnaya separatsiya poleznykh iskopaemykh* (*Gravity Separation of Minerals*). Dnepropetrovsk; 2003. 123 p. (in Russ.).
6. Rudyak V.Ya. Morden status of researches on nanofluids viscosity. *Vestnik Novosibirskogo gosudarstvennogo universiteta. Seriya: Fizika = Vestnik NSU. Series: Physics*. 2015;10(1):5–22 (in Russ.).
7. Batchelor G.K. Brownian diffusion of particles with hydrodynamic interaction. *J. Fluid Mechanics.* 1976;74(1): 1–29. https://doi.org/10.1017/S0022112076001663
8. Shkolnikov E.I., Grigorenko A.V., Lipatova I.A., Kumar V., Vlaskin M.S. Methane Impurity Effect in the Acetylene Decomposition on Size and Morphology of the Appearing Soot Particles. *Vestnik MGTU im. N.E. Baumana. Ser. Estestvennye nauki = Herald of the Bauman Moscow State Technical University. Series Natural Sciences*. 2023;2(107): 110–125 (in Russ.). http://doi.org/10.18698/1812-3368-2023-2-110-125
9. Likhanov V.A., Lopatin O.P., Kozlov A.N. Modeling soot formation in cylinder of diesel engine. *Nauchno-tekhnicheskie vedomosti SPbPU. Estestvennye i inzhenernye nauki = St. Petersburg Polytechnic University Journal of Engineering Science and Technology*. 2019;25(1):47–59 (in Russ.). https://doi.org/10.18721/JEST.25105
10. Naumenko O.F., Yur G.S., Results of a numerical study of the process of blowing suspended particles of diesel soot in a disturbed gas environment. *Polzunovskiy Vestnik.* 2006;4: 128–130 (in Russ.).
11. Rudnev B.I., Povalikhina O.V. Optical Parameters of Soot Particles and Parameters of Radiative Heat Exchange in Diesel Engine Combustion Chamber. *Vestnik TOGU = Bulletin of PNU*. 2014;2(33):133–140 (in Russ.).
12. Rudnev B.I., Povalikhina O.V. Diesel soot of nanostructure particles. *Nauchnye trudy Dal'rybvtuza = Scientific Journal of DALRYBVTUZ*. 2015;36:86–92 (in Russ.).
13. Shurupov S.V. Regularities of formation of dispersed carbon during isothermal pyrolysis of hydrocarbon raw materials. *Gazokhimiya.* 2009;9:64–72 (in Russ.).
14. Yurlov A.S. Physical properties, composition and structure of soot particles formed in the diesel engine cylinder. *Vestnik Vyatskogo GATU = Bulletin of Vyatka State Agrarian University*. 2023;4(18):253–261 (in Russ.).

СПИСОК ЛИТЕРАТУРЫ

1. Анисимов И.Г. и др. *Топлива, смазочные материалы, технические жидкости. Ассортимент и применение*: справочник; под ред. В.М. Школьникова. М.: Издательский центр «Техинформ»; 1999. 596 с. ISBN 5-89551-006-X
2. Матвеенко В.Н., Кирсанов Е.А. Вязкость и структура дисперсных систем. *Вестник Московского университета. Сер. 2. Химия.* 2011;52(4):243–276.
3. Бретшнайдер С. *Свойства газов и жидкостей. Инженерные методы расчета*: пер. с польск. М., Л.: Химия; 1966. 535 с.
4. Келбалиев Г.И., Расулов Р.С., Тагиев Д.Б. *Механика и реология нефтяных дисперсных систем*. М.: Маска; 2017. 462 с.
5. Пилов П.И. *Гравитационная сепарация полезных ископаемых*. Днепропетровск: Национальный горный университет; 2003. 123 с.
6. Рудяк В.Я. Современное состояние исследований вязкости наножидкостей. *Вестник Новосибирского государственного университета. Серия: Физика*. 2015;10(1):5–22.
7. Batchelor G.K. Brownian diffusion of particles with hydrodynamic interaction. *J. Fluid Mechanics.* 1976;74(1): 1–29. https://doi.org/10.1017/S0022112076001663
8. Школьников Е.И., Григоренко А.В., Липатова И.А., Кумар В., Власкин М.С. Влияние примеси метана при разложении ацетилена на размер и морфологию частиц образующейся сажи. *Вестник МГТУ им. Н.Э. Баумана. Сер. Естественные науки.* 2023;2(107):110–125. https://doi.org/10.18698/1812-3368-2023-2-110-125
9. Лиханов В.А., Лопатин О.П., Козлов А.Н. Моделирование сажеобразования в цилиндре дизеля. *Научно-технические ведомости СПбПУ. Естественные и инженерные науки*. 2019;25(1):47–59. https://doi.org/10.18721/JEST.25105
10. Науменко О.Ф., Юр Г.С. Результаты численного исследования процесса обдува взвешенных частиц дизельной сажи возмущенной газовой средой. *Ползуновский вестник*. 2006;4:128–130.
11. Руднев Б.И., Повалихина О.В. Оптические параметры частиц сажи и характеристики радиационного теплообмена в камере сгорания дизеля. *Вестник Тихоокеанского государственного университета* (*Вестник ТОГУ*). 2014;2(33):133–140.
12. Руднев Б.И., Повалихина О.В. Наноструктуры частиц дизельной сажи. *Научные труды Дальрыбвтуза*. 2015;36: 86–92.
13. Шурупов С.В. Закономерности образования дисперсного углерода при изотермическом пиролизе углеводородного сырья. *Газохимия*. 2009;9:64–72.
14. Юрлов А.С. Физические свойства, состав и структура частиц сажи, образующихся в цилиндре дизельного двигателя. *Вестник Вятского ГАТУ*. 2023;4(18):253–261.
15. Гюльмисарян Т.Г., Капустин В.М., Левенберг И.П. *Технический углерод: морфология, свойства, производство*. М.: Изд-во «Каучук и резина»; 2017. 586 с.
16. Раздьяконова Г.И., Лихолобов В.А., Кохановская О.А. *Технологии модификации технического углерода*: монография. Омск: Изд-во ОмГТУ; 2017. 160 с. ISBN 978-5-8149-2437-7
17. Стебелева О.П., Кашкина Л.В., Вшивкова О.А. Структура и морфология сажевых частиц, образующихся при испарении водных суспензий. *Российские нанотехнологии*. 2022;17(4):465–471. https://doi.org/10.56304/S1992722322040252

15. Gyulmisaryan T.G., Kapustin V.M., Levenberg I.P. *Tekhnicheskii uglerod: morfologiya, svoistva, proizvodstvo* (*Carbon Black: Morphology, Properties, Production*). Moscow: Kauchuk i rezina; 2017. 586 p. (in Russ.).
16. Razdiakonova G.I., Likholobov V.A., Kohanovskaya O.A. *Tekhnologii modifikatsii tekhnicheskogo ugleroda* (*Carbon Black Modification Technologies*): monograph. Omsk: OmSTU; 2017. 160 p. (in Russ.). ISBN 978-5-8149-2437-7
17. Stebeleva O.P., Kashkina L.V., Vshivkova O.A. Structure and morphology of carbon-black particles formed during the evaporation of aqueous suspensions. *Nanotechnol. Russia*. 2022;17(4):489–494. https://doi.org/10.1134/s2635167622040255
[Original Russian Text: Stebeleva O.P., Kashkina L.V., Vshivkova O.A. Structure and morphology of carbon-black particles formed during the evaporation of aqueous suspensions. *Rossiiskie nanotekhnologii*. 2022;17(4):465–471 (in Russ.). https://doi.org/10.56304/S1992722322040252]

About the authors

Anatoly V. Lesin, Researcher, A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences (TIPS RAS) (29, Leninskii pr., Moscow, 119991, Russia). E-mail: lesinav@ips.ac.ru. RSCI SPIN-code 7729-5478, https://orcid.org/0000-0002-1686-8125

Alexander V. Isaev, Dr. Sci. (Eng.), Leading Researcher, A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences (TIPS RAS) (29, Leninskii pr., Moscow, 119991, Russia). E-mail: a_isaev@ips.ac.ru. RSCI SPIN-code 7271-4416, https://orcid.org/0009-0004-7139-7524

Boris P. Tonkonogov, Dr. Sci. (Chem.)**,** Professor, Head of the Department of Chemistry and Technology of Lubricants and Chemmotology, Gubkin University (65/1, Leninskii pr., Moscow, 119991, Russia). E-mail: bpt734@gmail.com. Scopus Author ID 6506284001, ResearcherID B-7698-2018, https://orcid.org/0000-0003-1141-0120

Sergey V. Dunaev, Cand. Sci. (Mil.), Leading Researcher, A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences (TIPS RAS) (29, Leninskii pr., Moscow, 119991, Russia). E-mail: dunaevsv@ips.ac.ru. RSCI SPIN-code 1969-5765, https://orcid.org/0000-0001-6939-8713

Albert B. Kulikov, Cand. Sci. (Chem.), Deputy Director, A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences (TIPS RAS) (29, Leninskii pr., Moscow, 119991, Russia). E-mail: akulikov@ips.ac.ru. Scopus Author ID 7103153889, ResearcherID A-8738-2014, RSCI SPIN-code 3258-4823, https://orcid.org/0000-0003-1756-282X

Об авторах

Лесин Анатолий Викторович, научный сотрудник, ФГБУН Ордена Трудового Красного Знамени Институт нефтехимического синтеза им. А.В. Топчиева, Российская академия наук (ИНХС РАН) (119991, Россия, Москва, Ленинский пр., д. 29). E-mail: lesinav@ips.ac.ru. SPIN-код РИНЦ 7729-5478, https://orcid.org/0000-0002-1686-8125

Исаев Александр Васильевич, д.т.н., ведущий научный сотрудник, ФГБУН Ордена Трудового Красного Знамени Институт нефтехимического синтеза им. А.В. Топчиева, Российская академия наук (ИНХС РАН) (119991, Россия, Москва, Ленинский пр., д. 29). E-mail: a_isaev@ips.ac.ru. SPIN-код РИНЦ 7271-4416, https://orcid.org/0009-0004-7139-7524

Тонконогов Борис Петрович, д.х.н., профессор, заведующий кафедрой химии и технологии смазочных материалов и химмотологии, ФГАОУ ВО «Российский государственный университет нефти и газа (национальный исследовательский университет) им. И.М. Губкина» (119991, Россия, Москва, Ленинский пр., д. 65, корп. 1). E-mail: bpt734@gmail.com. Scopus Author ID 6506284001, ResearcherID B-7698-2018, https://orcid.org/0000-0003-1141-0120

Дунаев Сергей Васильевич, к.воен.н., ведущий научный сотрудник, ФГБУН Ордена Трудового Красного Знамени Институт нефтехимического синтеза им. А.В. Топчиева, Российская академия наук (ИНХС РАН) (119991, Россия, Москва, Ленинский пр., д. 29). E-mail: dunaevsv@ips.ac.ru. SPIN-код РИНЦ 1969-5765, https://orcid.org/0000-0001-6939-8713

Куликов Альберт Борисович, к.х.н., заместитель директора, ФГБУН Ордена Трудового Красного Знамени Институт нефтехимического синтеза им. А.В. Топчиева, Российская академия наук (ИНХС РАН) (119991, Россия, Москва, Ленинский пр., д. 29). E-mail: akulikov@ips.ac.ru. Scopus Author ID 7103153889, ResearcherID A-8738-2014, SPIN-код РИНЦ 3258-4823, https://orcid.org/0000-0003-1756-282X

Translated from Russian into English by N. Isaeva
Edited for English language and spelling by Dr. David Mossop

Tonkie Khimicheskie Tekhnologii = Fine Chemical Technologies.
2024;19(6):497–507 ISSN 2686-7575 (Online)

UDC 661.723.097.3:546.733
https://doi.org/10.32362/2410-6593-2024-19-6-497-507
EDN BWUXJG

CC BY

Highly efficient catalytic system for liquid-phase oxidation of 1-chloro-*n*-hexadecane with atmospheric oxygen

Valentin N. Sapunov[1], Yuriy L. Zotov[2,✉], Nguyen Thanh Tung[2], Yuriy V. Popov[2], Evgeniy V. Shishkin[2]

[1] *Mendeleev University of Chemical Technology of Russia, Moscow, 125047 Russia*

[2] *Volgograd State Technical University, Volgograd, 400005 Russia*

✉ *Corresponding author, e-mail: ylzotov@mail.ru*

Abstract

Objectives. To develop a highly efficient catalytic system for the liquid-phase oxidation of long-chain mono-chlorinated alkanes by oxygen in air to a mixture of high-boiling chlorinated carboxylic acids, which can serve as raw materials for the production of multifunctional additives for polyvinyl chloride.

Methods. The liquid-phase oxidation of 1-chloro-*n*-hexadecane by oxygen in air in the presence of a two-component catalytic system of $St_2Co(OH)$ and *N*-hydroxyphthalimide (*N*-HPI) was investigated. The air flow rate during the oxidation of 1-chloro-*n*-hexadecane was controlled by a gas meter. Identification, composition, and content of the starting 1-chloro-*n*-hexadecane for conversion control were conducted using chromatographic-mass spectrometric analysis on an Agilent GC 7820A/MSD 5975 instrument. The structure of cobalt(III) hydroxystearate was confirmed by infrared spectroscopy.

Results. Investigation of a two-component catalytic system $St_2Co(OH)$–*N*-HPI in the oxidation reaction of 1-chloro-*n*-hexadecane by oxygen in air revealed that both components of the system participate in the formation of hydroperoxides. This accelerates their formation and contributes to high hydroperoxide content in the reaction mass. It was observed that $St_2Co(OH)$ in the two-component catalytic system accelerates the decomposition of hydroperoxides better than St_2Co in another two-component catalytic system previously studied, making it promising for application in the process. The oxides thus obtained can serve as raw materials for the production of multifunctional additives for polyvinyl chloride which could lead to improvements in the quality and properties of this material.

Conclusions. The investigation into the liquid-phase oxidation of 1-chloro-*n*-hexadecane by oxygen in air using the two-component catalytic system $St_2Co(OH)$–*N*-HPI has shown it to be more efficient compared to the two-component catalytic system St_2Co–*N*-HPI. The optimal concentration of the two-component catalytic system $St_2Co(OH)$–*N*-HPI in the reaction system for the liquid-phase oxidation of 1-chloro-*n*-hexadecane by oxygen in air has been determined to be 9 mol % of the raw material loading, with a molar ratio of components of 1 : 6. Such a catalytic system enables an acid number in the oxide of 42 mg KOH/g to be attained after 10 h of oxidation.

Keywords

1-chloro-*n*-hexadecane, liquid-phase catalytic oxidation, two-component catalytic system, cobalt hydroxystearate, *N*-hydroxyphthalimide, hydroperoxide, conversion, acid number, carboxylic acids

Submitted: 03.05.2024
Revised: 05.08.2024
Accepted: 17.10.2024

For citation

Sapunov V.N., Zotov Yu.L., Nguyen Th.T., Popov Yu.V., Shishkin E.V. Highly efficient catalytic system for liquid-phase oxidation of 1-chloro-*n*-hexadecane with atmospheric oxygen. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2024;19(6):497–507. https://doi.org/10.32362/2410-6593-2024-19-6-497-507

© V.N. Sapunov, Yu.L. Zotov, Nguyen Thanh Tung, Yu.V. Popov, E.V. Shishkin, 2024

НАУЧНАЯ СТАТЬЯ

Высокоэффективная каталитическая система для жидкофазного окисления 1-хлор-*н*-гексадекана кислородом воздуха

В.Н. Сапунов[1], Ю.Л. Зотов[2,✉], Нгуен Тхань Тунг[2], Ю.В. Попов[2], Е.В. Шишкин[2]

[1] *Российский химико-технологический университет им. Д.И. Менделеева, Москва, 125047 Россия*

[2] *Волгоградский государственный технический университет, Волгоград, 400005 Россия*

✉ *Автор для переписки, e-mail: ylzotov@mail.ru*

Аннотация

Цели. Разработка высокоэффективной каталитической системы для жидкофазного окисления длинноцепочечных монохлорированных алканов кислородом воздуха в смесь высококипящих хлорсодержащих карбоновых кислот, которые могут служить сырьем для получения многофункциональных добавок для поливинилхлорида.

Методы. Исследование жидкофазного окисления 1-хлор-*н*-гексадекана (1-ХГД) кислородом воздуха в присутствии двухкомпонентной каталитической системы, состоящей из $St_2Co(OH)$ и *N*-гидроксифталимида (*N*-ГФИ). Расход воздуха при окислении 1-ХГД контролировали газовым счетчиком. Идентификацию, состав и содержание исходного 1-ХГД для контроля конверсии проводили с использованием хромато-масс-спектрометрического анализа на приборе Agilent GC 7820A/MSD 5975. Строение гидроксистеарата кобальта(III) подтверждено инфракрасной спектроскопией.

Результаты. Исследование двухкомпонентной каталитической системы $St_2Co(OH)$–*N*-ГФИ в реакции окисления 1-ХГД кислородом воздуха показало, что оба компонента каталитической системы участвуют в процессе образования гидропероксидов, что значительно ускоряет их образование и способствует созданию высоких содержаний гидропероксидов в реакционной массе. Установлено, что $St_2Co(OH)$ в составе двухкомпонентной каталитической системы ускоряет реакцию разложения гидропероксидов лучше, чем St_2Co в составе изученной нами ранее двухкомпонентной каталитической системы St_2Co–*N*-ГФИ. Полученные оксидаты могут служить сырьем для создания многофункциональных добавок для переработки поливинилхлорида.

Выводы. Установлено, что для жидкофазного окисления 1-ХГД кислородом воздуха двухкомпонентная каталитическая система $St_2Co(OH)$–*N*-ГФИ является более эффективной, чем двухкомпонентная каталитическая система St_2Co–*N*-ГФИ. Найдено, что для жидкофазного окисления 1-ХГД кислородом воздуха оптимальное содержание двухкомпонентной каталитической системы $St_2Co(OH)$–*N*-ГФИ в реакционной массе составляет 9 мол. % от загрузки сырья при мольном соотношении компонентов 1 : 6. Такая каталитическая система позволяет получать кислотное число в оксидате 42 мгКОН/г через 10 ч окисления.

Ключевые слова

1-хлор-*н*-гексадекан, жидкофазное каталитическое окисление, двухкомпонентная каталитическая система, гидроксистеарат кобальта, *N*-гидроксифталимид, гидропероксид, конверсия, кислотное число, карбоновые кислоты

Поступила: 03.05.2024
Доработана: 05.08.2024
Принята в печать: 17.10.2024

Для цитирования

Сапунов В.Н., Зотов Ю.Л., Нгуен Т.Т., Попов Ю.В., Шишкин Е.В. Высокоэффективная каталитическая система для жидкофазного окисления 1-хлор-*н*-гексадекана кислородом воздуха. *Тонкие химические технологии*. 2024;19(6):497–507. https://doi.org/10.32362/2410-6593-2024-19-6-497-507

INTRODUCTION

We have previously shown that liquid-phase catalytic low-temperature oxidation of chlorinated paraffins and long-chain normal monohaloalkanes with atmospheric oxygen produces oxidates containing, among other things, carboxylic acids which can be used as multifunctional additives for processing polyvinyl chloride (PVC) [1–3]. Such multifunctional additives, as a rule, have low toxicity [4], exhibit the properties of plasticizers, stabilizers, lubricants, and impart useful properties to products based on PVC [5, 6]. Long-chain normal individual monohaloalkanes are also of interest when studying the regularities of processes occurring during their catalytic liquid-phase oxidation. In this case the reaction and composition of the reaction mass are significantly simplified when compared to the oxidation of chlorinated paraffins [3],

which are mixtures of chloroalkanes with varying degrees of chlorination.

There is insufficient data in the literature on the oxidation of individual long-chain chlorinated hydrocarbons in the liquid phase with atmospheric oxygen in the presence of organic cobalt salts. Thus, the search for highly effective catalytic systems for aerobic oxidation of long-chain chlorinated alkanes is currently important for theory and practice.

Previously, we used a cobalt(II) stearate catalyst (St_2Co, St = $C_{17}H_{35}COO$–) [7] and a catalytic system consisting of St_2Co and *N*-hydroxyphthalimide (*N*-HPI) [8] for the liquid-phase oxidation of 1-chloro-*n*-hexadecane (1-CHD) with atmospheric oxygen to carboxylic acids.

The aim of this study is to develop a highly effective catalytic system for the liquid-phase oxidation of long-chain monochlorinated alkanes with atmospheric oxygen to a mixture of high-boiling chlorine-containing carboxylic acids which can be used as a raw material for obtaining multifunctional additives for PVC. This catalytic system should be capable of performing oxidation with high conversion, high rate and allow products with high acid number values to be obtained. For this purpose, we have developed a new catalytic system containing $St_2Co(OH)$ and *N*-HFI using the example of 1-CHD oxidation [9]. During oxidation with atmospheric oxygen this system allows a reaction mass (oxidate) to be obtained which contains mainly carboxylic acids, esters, and alcohols with a maximum content of high-boiling chlorine-containing carboxylic acids.

MATERIALS AND METHODS

In this work, we used 1-CHD (*Alfa Aesar*, CAS 4860-03-1, USA). *N*-HPI (*Acros Organics*, CAS 524-38-9, USA), cobalt(II) stearate (*Alfa Aesar*, CAS 1002-88-6, USA), and cobalt(III) hydroxystearate prepared according to the method [10] were used as catalysts. The latter method allows cobalt(III) hydroxystearate to be obtained with a yield of 87–88%.

The infrared spectrum of cobalt(III) hydroxystearate is as follows: ν = 3360–3320 cm^{-1}, (s), stretching vibrations of the OH group; 2970 cm^{-1}, (s), stretching vibrations of CH_3–; 2850–2815 and 2940–2915 cm^{-1}, stretching vibrations of CH_2 groups; 1480 cm^{-1}, (s), deformation vibrations of –CH_2–; 720 cm^{-1}, (s), rocking vibrations of –$(CH_2)_n$–; 1710 cm^{-1}, (m), stretching vibrations of the carbonyl group ν(C=O); 1580 cm^{-1}, (s), stretching vibrations of COO^- in carboxylic acid salts; 1410 cm^{-1}, (s), deformation vibrations of –CH_2–CO; 580 cm^{-1}, (c), stretching vibrations of Co–O bonds. The spectrum of the salt obtained does not contain absorption bands in the region of 1630–1600 cm^{-1}, as characteristic of coordination or crystallization water.

The oxidation of 1-CHD was carried out in a 150-mL glass column reactor with a length to diameter ratio of 10 : 1 at a specific air flow rate of 65 L/(min · kg of substrate) or more [11]. The initial filling of the reactor volume with the reaction mixture was 46% (69.36 mL). The content of the catalytic system varied from 6 to 12 mol % in the feedstock at a molar ratio of components in the catalytic system of 1 : 6. The results of the studies showed that the repeated use of the St_2Co–*N*-HPI catalytic system decreases the acid number from 26.8 to 10 mg of KOH/g while decreasing the conversion from 21.2 to 8%. The repeated use of the $St_2Co(OH)$–*N*-HPI catalytic system decreases the acid number from 41 to 15 mg of KOH/g, while decreasing the conversion from 31 to 14% after 10 h of oxidation. Thus, a fresh catalytic system was used in all experiments.

The air flow from the compressor was controlled by a gas meter. Air distribution in the reaction mass was carried out by a bubbler with a porous glass diaphragm (porosity 160 μm). Before feeding air into the reactor, it was heated to a reaction temperature of 105°C. As shown previously [11], the operation of the column apparatus switches from the bubbling mode to the foam mode under experimental conditions starting with an air flow rate of 65 L/(min · kg of substrate) and more. The foam mode has the highest specific contact surface, allowing the process to be carried out without diffusional resistance in the kinetic region.

The scheme of the laboratory setup is shown in Fig. 1.

The reactor unit allows light oxidation products carried away by air from the reaction volume to be collected. The exhaust air is bubbled through distilled water to absorb acidic reaction products. In order to avoid breakthrough and maintain a low concentration of absorbed products in the absorbers, the absorbent was replaced with a new portion every 30 min. The acid number was determined for the oxidate in the reactor and for the aqueous solution in the absorbers. The error in determining the acid number of higher carboxylic acids according to GOST 22386-77[1] is 1%.

The identification, composition and content of the initial 1-CHD for conversion control were performed by means of chromatography-mass spectrometric analysis on an Agilent GC 7820A/MSD 5975 instrument

[1] GOST 22386-77. State Standard of the USSR. Synthetic fatty acids and alcohols. Method for determining acid number. Moscow: State Committee of Standards of the Council of Ministers of the USSR, 1978. 10 p.

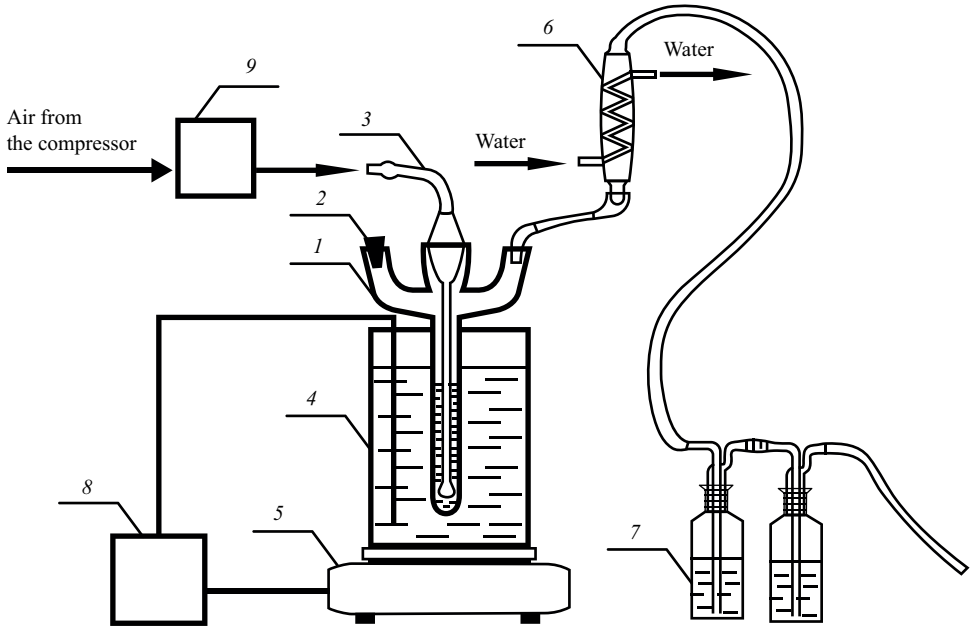


Fig. 1. Setup for liquid-phase oxidation of hexadecane and 1-chlorohexadecane
(*1*) bubbling reactor, column type, length to diameter ratio 10 : 1;
(*2*) fitting for sampling;
(*3*) bubbler;
(*4*) glycerol bath;
(*5*) heating element;
(*6*) refrigerator-condenser,
(*7*) absorber,
(*8*) electronic reactor temperature control unit, and
(*9*) air heating

(*Agilent Technologies*, USA) with a 5-MS quartz capillary column 30 m long, 0.25 mm in diameter. The carrier gas was helium, 1.0 mL/min; injector with a 1 : 5 flow splitter; and injector temperature: 250°C. When programming the capillary column temperature, the initial temperature was 80°C, final temperature, 280°C, isotherm time 10 min; temperature rise rate 10°C/min; and total analysis time 30 min. The detector was a quadrupole mass spectrometer using electron impact ionization with an electron energy of 70 eV in the full mass spectrum scanning mode. The quadrupole temperature was 150°C, and the source temperature was 230°C.

It was found that chlorine was not split off during the oxidation process either from the initial chloroalkane or from the reaction products, i.e., chloracids were present in the oxidate [7]. The acids absorbed in the traps were only derivatives of low-molecular alkanes.

The content of hydroperoxides (wt %) in the reaction mass during oxidation was determined using the method [12]. The accuracy of the analysis was 5% of the relative error of determination [13].

RESULTS AND DISCUSSION

Previously in the process of studying the aerobic oxidation of 1-CHD to carboxylic acids, we developed a two-component catalytic system consisting of cobalt stearate (St_2Co) and *N*-HPI [8]. The optimal molar ratio of the components was found to be 1 : 6. The best results for the acid number in the oxidate (up to 25 mg·KOH/g [8]) were obtained with a content of this catalytic system of 6 mol % in the feedstock, a temperature of 105°C, and an air flow rate of 65 L/(min · kg of substrate) for 5 h of oxidation [8, 11].

Carrying out the oxidation process of 1-CHD under the same conditions, but using a new catalytic system consisting of cobalt hydroxystearate $St_2Co(OH)$ and *N*-HPI, as before, in a molar ratio of 1 : 6, produced better results. Data on the variants of the catalytic system is presented in Table 1, and the results of the experiments, in Fig. 2. For comparison, this figure shows the kinetic curves of 1-CHD oxidation in the presence of the St_2Co–*N*-HPI catalytic system. The data was obtained in [8].

The change in the conversion of 1-CHD over time during its oxidation with atmospheric oxygen at different

Table 1. Variants of the two-component catalytic system $St_2Co(OH)$–*N*-hydroxyphthalimide (*N*-HPI) for the oxidation of 1-chlorohexadecane with air

Characteristics	Experiments			
	1	2	3	4
1-CHD, g	60			
Molar ratio of $St_2Co(OH)$/*N*-HPI in the catalytic system	1 : 6			
Mass content of the catalytic system in the feedstock, wt %	5.3	6.7	7.9	10.6
Molar content of the catalytic system in the feedstock, mol %	6	7.5	9	12
Molar content of the cobalt hydroxystearate catalyst $St_2Co(OH)$, mol % in the catalytic system	0.86	1.07	1.29	1.71
Molar content of the *N*-HPI catalyst, mol % in the catalytic system	5.14	6.43	7.71	10.29

molar contents of catalytic systems in the feedstock is shown in Fig. 2.

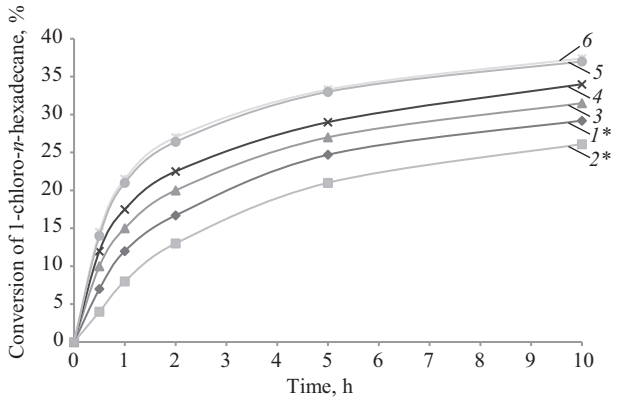


Fig. 2. Dependence of the conversion of 1-chlorohexadecane on time during its oxidation with atmospheric oxygen in the presence of two-component catalytic systems (curves *1** and *2** for the St_2Co–*N*-HPI catalytic system and curves *3*–*6* for the $St_2Co(OH)$–*N*-HPI catalytic system) with their different molar content in raw materials. (*1**) 6; (*2**) 9; (*3*) 6; (*4*) 7.5; (*5*) 9; (*6*) 12 mol % of raw material loading

Comparison of the kinetic curves presented in Fig. 2 shows a significant advantage of the $St_2Co(OH)$–*N*-HPI catalytic system over the St_2Co–*N*-HPI catalytic system. Increasing the content of the $St_2Co(OH)$–*N*-HPI catalytic system from 3 to 9 mol % leads to an increase in the rate of liquid-phase oxidation of 1-CHD and an increase in its conversion over 10 h of the process from 29.2% to 37%. Increasing the content of the new catalytic system over 9 mol % of the feedstock load does not lead to a further increase in the rate of 1-CHD oxidation.

The oxidation of hydrocarbons with atmospheric oxygen to carboxylic acids is known to be a multi-stage process. The result of the first stage of oxidation is the formation of hydroperoxides [14]. The rate of their formation and consumption into intermediate products (alcohols, ketones, aldehydes, etc.) significantly depends on the catalytic systems used.

Figure 3 shows the dependencies of the conversion of 1-CHD and the content of hydroperoxides in the reaction mass on time during liquid-phase oxidation of 1-CHD in the presence of catalytic systems at their optimal content.

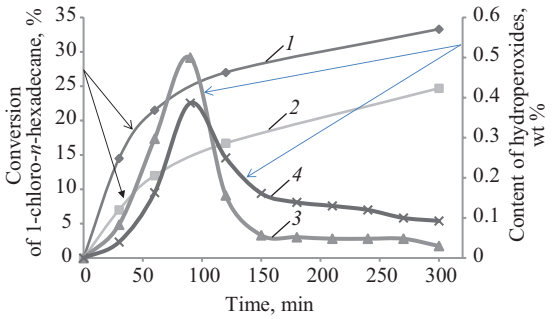


Fig. 3. Dependence of the conversion of 1-chloro-*n*-hexadecane (curves *1* and *2*) and the content of hydroperoxides (curves *3* and *4*) on time during the oxidation of 1-chloro-*n*-hexadecane in the presence of the found optimal content of catalytic systems. Curves *1*, *3* — 9 mol % of the feedstock load of a two-component catalytic system ($St_2Co(OH)$–*N*-HPI in a molar ratio of 1 : 6); *2*, *4* — 6 mol % of the feedstock load of a two-component catalytic system (St_2Co–*N*-HPI in a molar ratio of 1 : 6). Air consumption 65 L/(min·kg of substrate), temperature 105°C

Analysis of Fig. 3 shows that when using the two-component catalytic system $St_2Co(OH)$–*N*-HPI (curve *3*), the rate of hydroperoxide accumulation and consumption is significantly higher than when using the catalytic system St_2Co–*N*-HPI (curve *4*).

It also follows from Fig. 3 that when using the two-component catalytic system $St_2Co(OH)$–*N*-HPI, the average rate of 1-CHD consumption is higher (curve *1*) than in the presence of the catalytic system St_2Co–*N*-HPI (curve *2*). Comparison of curves *1* and *2* with curves *3* and *4* on the same graph shows that as the conversion of 1-CHD increases to 25% (curve *1*), the content of hydroperoxides increases to 0.5% (curve *3*). However, for the St_2Co–*N*-HPI catalytic system with a 1-CHD conversion of 15% (curve *2*), the content of hydroperoxides is only 0.4% (curve *4*).

When using the two-component $St_2Co(OH)$–*N*-HPI catalytic system, the rapid accumulation of hydroperoxides is due to the fact that both *N*-HPI and $St_2Co(OH)$ participate in the chain initiation stage. Both components promote the formation and increase in the concentration of the phthalimide *N*-oxyl radical PINO$^\bullet$. As a result, the formation of hydroperoxides is accelerated and their content in the reaction mass increases.

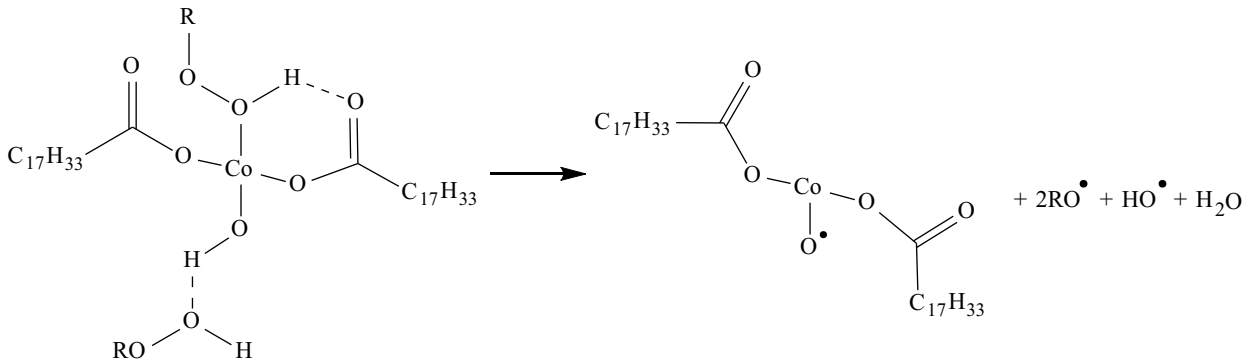
The presence of *N*-HPI in the reaction system also has a significant effect on the selectivity of hydroperoxide formation [15]. Peroxide radicals (ROO$^\bullet$) quickly react with the initial *N*-HPI molecule, thus forming hydroperoxide and *N*-oxyl radical PINO$^\bullet$.

Thus, a decrease in the concentration of peroxide radicals (ROO$^\bullet$) reduces the rate of quadratic chain termination, significantly increasing the selectivity of hydroperoxide formation and, accordingly, reducing the rate of byproduct formation [15].

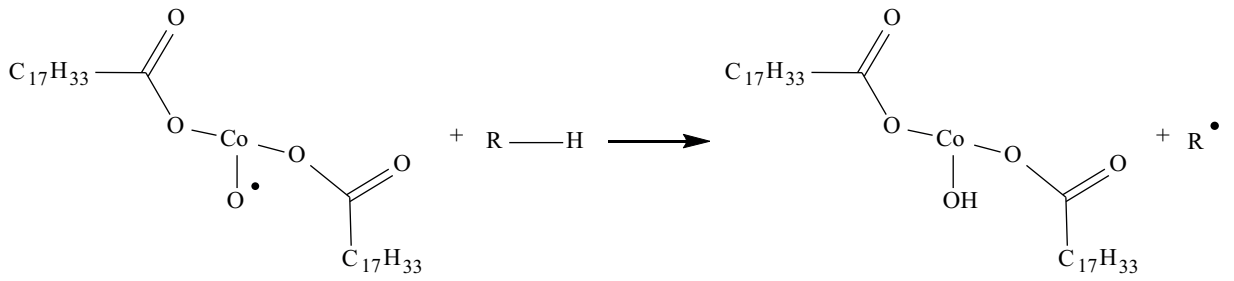
In the presence of the $St_2Co(OH)$–*N*-HPI catalytic system, hydroperoxides were found to decompose more quickly compared to the St_2Co–*N*-HPI catalytic system (Fig. 3). The increase in the rate of hydroperoxides decomposition under the action of the catalytic system $St_2Co(OH)$–*N*-HPI appears to be due to the fact that $St_2Co(OH)$ can participate in the process of hydroperoxides decomposition by forming hydrogen bonds with two hydroperoxide molecules: one hydroperoxide molecule forms a hydrogen bond with carbonyl oxygen, and the second forms a hydrogen bond of the hydroperoxide molecule with the –OH group of $St_2Co(OH)$ (Scheme 1) [16].

The resulting radical $CoSt_2O^\bullet$ quickly transforms into $CoSt_2(OH)$ by interacting with the raw material molecule (Scheme 2).

A mixture of oxygen-containing products (ketones, aldehydes, etc.) is known to be formed in the process of hydroperoxides decomposition. After oxidation, they are converted into carboxylic acids [14]. Figure 4 shows the dependence of the acid number in the oxidate on time.



Scheme 1. Decomposition of hydroperoxides involving $CoSt_2(OH)$



Scheme 2. Regeneration of $CoSt_2(OH)$

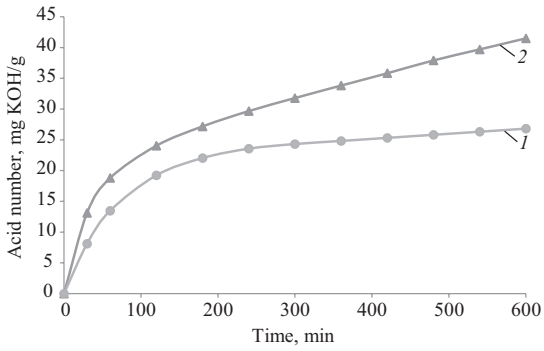


Fig. 4. Dependence of the acid number in the oxidate on time during the oxidation of 1-chlorohexadecane in the presence of catalytic systems: (*1*) 6 mol % of the feedstock load of a two-component catalytic system (St_2Co–*N*-HPI in a molar ratio of 1 : 6); (*2*) 9 mol % of the feedstock load of a two-component catalytic system ($St_2Co(OH)$–*N*-HPI in a molar ratio of 1 : 6). Air consumption 65 L/(min · kg of substrate), temperature 105°C

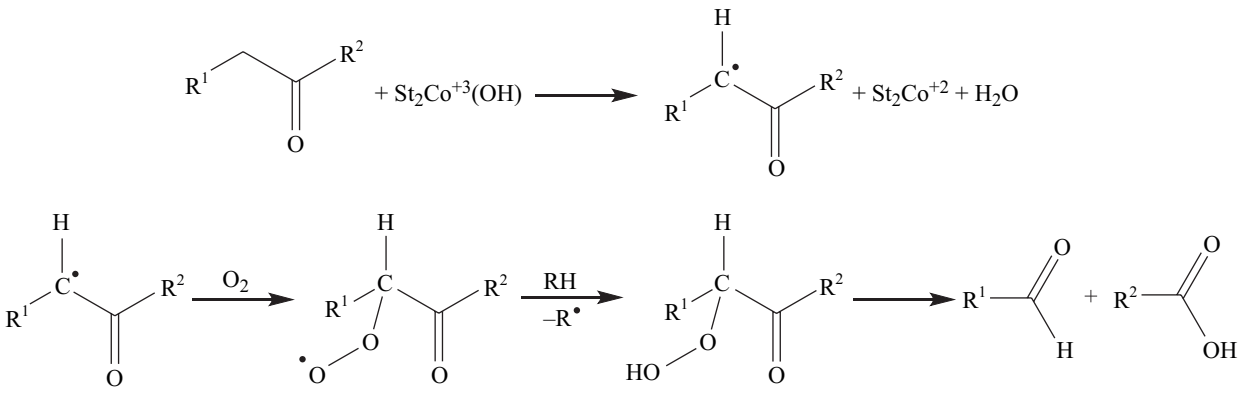
Figure 4 shows that the use of the $St_2Co(OH)$–*N*-HPI catalytic system enables a higher content of carboxylic acids to be obtained at a higher rate than in the presence of the St_2Co–*N*-HPI catalytic system.

Ishii [17] points out that, for example, when oxidizing cyclohexane using the Co(III) catalyst instead of Co(II) at close conversion values, the selectivity of the products (ketones and acids) is always higher. This fact can be explained by the ability of $St_2Co^{+3}(OH)$, as part of the $St_2Co^{+3}(OH)$–*N*-HPI catalytic system, to accelerate the oxidation of intermediate products, for example, ketones into acids according to Scheme 3.

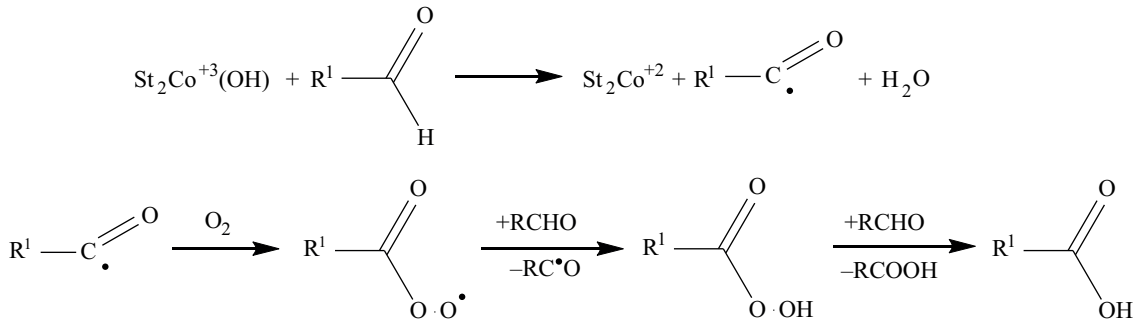
Further, the resulting aldehydes yield acids upon oxidation in the presence of $St_2Co(OH)$ according to Scheme 4.

It has been shown experimentally that the oxidate contains chlorinated and non-chlorinated carboxylic acids (Table 2) in accordance with the presented transformation schemes.

Thus, the presence of $St_2Co(OH)$ in the catalytic system $St_2Co(OH)$–*N*-HPI promotes the acceleration of the formation and consumption of hydroperoxides into intermediate products (ketones, aldehydes, etc.) and their secondary oxidation into carboxylic acids. We also considered 1-CHD, a solvent, as a factor in accelerating the oxidation process. Polar 1-CHD is known to improve the solubility of *N*-HPI [18] while worsening the conditions for micelle formation from cobalt salts, thus enhancing the activity of the catalyst [14].



Scheme 3. Oxidation of intermediate products (ketones) to acids involving $St_2Co(OH)$



Scheme 4. Oxidation of intermediate products (aldehydes) to acids involving $St_2Co(OH)$

Table 2. Composition of acids isolated from the oxidate after 5 h of 1-chloro-*n*-hexadecane oxidation with air in the presence of the catalytic system $St_2Co(OH)$ *N*-HPI

Acids	Molecular weight, *M*, g/mol	Content, %
$CH_3–(CH_2)_{13}–COOH$	242	5.56
$CH_3–(CH_2)_{12}–COOH$	228	1.79
$CH_3–(CH_2)_{11}–COOH$	214	1.49
$CH_3–(CH_2)_{10}–COOH$	200	7.44
$CH_3–(CH_2)_9–COOH$	186	11.71
$CH_3–(CH_2)_8–COOH$	172	14.41
$CH_3–(CH_2)_7–COOH$	158	13.93
$CH_3–(CH_2)_6–COOH$	144	10.38
$Cl–(CH_2)_9–COOH$	206.5	10.89
$Cl–(CH_2)_{10}–COOH$	220.5	8.53
$Cl–(CH_2)_{11}–COOH$	234.5	8.04
$Cl–(CH_2)_{12}–COOH$	248.5	5.84

CONCLUSIONS

The study established that the two-component catalytic system $St_2Co(OH)$–*N*-HPI is more effective for the liquid-phase oxidation of 1-CHD with atmospheric oxygen than the two-component catalytic system St_2Co–*N*-HPI.

The optimal content of the two-component catalytic system $St_2Co(OH)$–*N*-HPI in the reaction system for liquid-phase oxidation of 1-CHD with atmospheric oxygen was found to be 9 mol % of the feedstock load, with a molar ratio of components of 1 : 6. Such a catalytic system enables an acid number in the oxidate of 42 mgKOH/g to be obtained after 10 h of oxidation.

Acknowledgments

The work was performed using the equipment of the Center for Collective Use "Physicochemical methods of Analysis" at the Volgograd State Technical University.

Authors' contributions

V.N. Sapunov—design of the research concept, discussion and analysis of the results.

Yu.L. Zotov—design of the research concept, development of the experiment, discussion and analysis of the results, writing the text of the article.

Nguyen Thanh Tung—design of the research concept, planning and conducting experimental studies, processing the data obtained, preparation of the data obtained for publication.

Yu.V. Popov—consultation on conducting individual stages of the study, scientific editing.

E.V. Shishkin—consultation on conducting individual stages of the study, scientific editing.

The authors declare no conflicts of interest.

REFERENCES

1. Zotov Yu.L., Krasil'nikova K.F., Popov Yu.V., Butakova N.A., Vasichkina E.V., Borshcheva V.N. *Method of Obtaining Higher Fatty Chlorinated Acids*: RF Pat. RU 2526056. Publ. 20.08.2014 (in Russ).
2. Zotov Yu.L., Krasil'nikova K.F., Popov Yu.V., Butakova N.A., Erina E.V., Vasichkina E.V. *Polymer Composition for Cable Plastic*. RF Pat. RU 2520097. Publ. 20.06.2014 (in Russ).
3. Zotov Yu.L., Butakova N.A., Popov Yu.V. *Okislenie promyshlennykh khlorparafinov kislorodom vozdukha* (*Oxidation of Industrial Chlorinated Paraffins with Air Oxygen*). Monograph. Volgograd: VolgGTU; 2014. 123 p. (in Russ).
4. Zotov Yu.L., Kozlovtsev V.A., Erina E.V., *et al*. Multifunctional composition SINISTAD for polymers. XXIV. The use of the SINSTAD composition as a stabilizer in polymer compositions based on PVC and Poviden. *Plasticheskie Massy*. 2012;6: 55–56 (in Russ).
5. No B.I., Zotov Yu.L., Gora A.V. Multifunctional composition SINISTAD for polymers. XIV. Study of the oxidation process of chlorinated paraffin HP-30. *Plasticheskie Massy*. 2003;6:34–35 (in Russ).
6. Zotov Yu.L., Zapravdina D.M., Zotova N.Yu., Tsysar' D.S. Multifunctional composition SINISTAD for polymers. In: *The 5th International Conference-School on Chemical Technology: Collection of Abstracts of Reports of the Satellite Conference of the 20th Mendeleev Congress on General Applied Chemistry.* V. 1. Volgograd; 2016. P. 414–415 (in Russ).
7. Zotov Yu.L., Butakova N.A., Borshcheva V.N., Panov A.O. Oxidation of 1-chlorohexadecane with atmospheric oxygen in the presence of cobalt. *Izvestiya VolgGTU = Izvestia VSTU. Series Chemistry and Technology of Hetero-Organic Monomers and Polymer Materials*. 2014;7(134):66–70 (in Russ).
8. Zotov Yu.L., Shishkin E.V., Nguen T.T., Shipaeva T.A. Catalytic system for the oxidation of 1-chlorohexadecane with atmospheric oxygen. *Khimicheskaya promyshlennost' segodnya = Chemical Industry Developments*. 2023;2:23–30 (in Russ).
9. Zotov Yu.L., Lashko D.A., Shishkin E.V., Nguen T.T. *Method of Producing Higher Fatty Chlorinated Acids*: RF Pat. RU 2768727. Publ. 24.03.2022 (in Russ).
10. Zotov Yu.L., Krasilnikova K.F., Popov Yu.V., Panov A.O., Burtsev A.A., Konnova A.A. *Method of Producing Higher Fatty Chlorinated Acids*: RF Pat. RU 2586071. Publ. 10.06.2016 (in Russ).
11. Zotov Yu.L., Shishkin E.V., Nguen T.T. Study of the influence of air consumption on the process of catalytic oxidation of monochlorinated long-chain hydrocarbons. *Izvestiya VolgGTU = Izvestia VSTU. Series Chemistry and Technology of Hetero-Organic Monomers and Polymer Materials*. 2022;5(264):25–32 (in Russ.).
12. Odabashyan G.V., Shvets V.F. *Laboratornyi praktikum po khimii i tekhnologii osnovnogo organicheskogo i neftekhimicheskogo sinteza* (*Laboratory Workshop on Chemistry and Technology of Basic Organic and Petrochemical Synthesis*). Moscow: Khimiya; 1992. 240 p. (in Russ.).
13. Vashchenkov I.S., Verzhichinskaya S.V., Grechishkina O.S., Karadzhev M.A., Petina E.S. Analysis of organic peroxides by potentiometric titration. *Uspekhi v Khimii i Khimicheskoi Tekhnologii*. 2014;28(10):10–13 (in Russ.).
14. Emanuel N.M., Denisov E.T., Maizus Z.K. *Tsepnye reaktsii okisleniya uglevodorodov v zhidkoi faze* (*Chain Reactions of Hydrocarbon Oxidation in the Liquid Phase*). Moscow: Nauka; 1965. 375 p. (in Russ.).

СПИСОК ЛИТЕРАТУРЫ

1. Зотов Ю.Л., Красильникова К.Ф., Попов Ю.В., Бутакова Н.А., Васичкина Е.В., Борщева В.Н. *Способ получения высших жирных хлорированных кислот*: пат. RU 2526056 РФ. Заявка № 2013121870/04; заявл. 15.05.2013; опубл. 20.08.2014. Бюл. № 23.
2. Зотов Ю.Л., Красильникова К.Ф., Попов Ю.В., Бутакова Н.А., Ерина Е.В., Васичкина Е.В. *Полимерная композиция для кабельного пластиката*: пат. RU 2520097 РФ. Заявка № 20121581129/04; заявл. 28.12.2012; опубл. 20.06.2014. Бюл. № 17.
3. Зотов Ю.Л., Бутакова Н.А., Попов Ю.В. *Окисление промышленных хлорпарафинов кислородом воздуха:* монография. Волгоград: Изд. ВолгГТУ; 2014. 123 с.
4. Зотов Ю.Л., Козловцев В.А., Ерина Е.В., Куляева В.А., Тростянская М.Б., Шаврина О.Ю. Многофункциональная композиция «СИНИСТАД» для полимеров. XXIV. Использование композиции «СИНСТАД» в качестве стабилизатора в полимерных композициях на основе ПВХ и «Повидена». *Пластические массы*. 2012;6:55–56.
5. Но Б.И., Зотов Ю.Л., Гора А.В. Многофункциональная композиция «СИНСТАД» для полимеров. XIV. Изучение процесса окисления хлорпарафина ХП-30. *Пластические массы*. 2003;6:34–35.
6. Зотов Ю.Л., Заправдина Д.М., Зотова Н.Ю., Цысарь Д.С. Многофункциональная композиция «СИНСТАД» для полимеров. В сб.: *V Международная конференция-школа по химической технологии: сборник тезисов докладов сателлитной конференции XX Менделеевского съезда по общей прикладной химии*. Т. 1. Волгоград; 2016. С. 414–415.
7. Зотов Ю.Л., Бутакова Н.А., Борщева В.Н., Панов А.О. Окисление 1-хлоргексадекана кислородом воздуха в присутствии стеарата кобальта. *Известия ВолгГТУ. Серия «Химия и технология элементоорганических мономеров и полимерных материалов».* 2014;7(134):66–70.
8. Зотов Ю.Л., Шишкин Е.В., Нгуен Т.Т., Шипаева Т.А. Каталитическая система для окисления 1-хлоргексадекана кислородом воздуха. *Химическая промышленность сегодня*. 2023;2:23–30.
9. Зотов Ю.Л., Лашко Д.А., Шишкин Е.В., Нгуен Т.Т. *Способ получения высших жирных хлорированных кислот*: пат. RU 2768727 РФ. Заявка № 2021110571; заявл. 15.04.2021; опубл. 24.03.2022.
10. Зотов Ю.Л., Красильникова К.Ф., Попов Ю.В., Панов А.О., Бурцев А.А., Коннова А.А. *Способ получения высших жирных хлорированных кислот*: пат. RU № 2586071 РФ. Заявка № 2015121176/04; заявл. 03.06.2015; опубл. 10.06.2016. Бюл. № 16
11. Зотов Ю.Л., Шишкин Е.В., Нгуен Т.Т. Исследование влияния расхода воздуха на процесс каталитического окисления монохлорированных длинноцепочечных углеводородов. *Известия ВолгГТУ. Серия «Химия и технология элементоорганических мономеров и полимерных материалов».* 2022;5(264):25–32.
12. Одабашян Г.В., Швец В.Ф. *Лабораторный практикум по химии и технологии основного органического и нефтехимического синтеза.* М.: Химия; 1992. 240 с.
13. Ващенков И.С., Вержичинская С.В., Гречишкина О.С., Караджев М.А., Петина Е.С. Анализ органических перекисных соединений методом потенциометрического титрования. *Успехи в химии и химической технологии*. 2014;28(10):10–13.
14. Эмануэль Н.М., Денисов Е.Т., Майзус З.К. *Цепные реакции окисления углеводородов в жидкой фазе*. М.: Наука; 1965. 375 с.

15. Sapunov V.N., Koshel' G.N., Rumyantseva Y.B., *et al.* The role of *N*-hydroxyphthalimide in the reaction mechanism of liquid-phase oxidation of *p*-cymene. *Pet. Chem.* 2013;53(3): 171–176. https://doi.org/10.1134/S0965544113030092 [Original Russian Text: Sapunov V.N., Koshel' G.N., Rumyantseva Yu.B., Kurganova E.A., Kukushkina N.D. The role of *N*-hydroxyphthalimide in the reaction mechanism of liquid-phase oxidation of *p*-cymene. *Neftekhimiya*. 2013;53(3):193–198 (in Russ.). https://doi.org/10.7868/S0028242113030106]
16. Perkel' A.L., Voronina S.G., Buneeva E.I., Nepomnyashchikh Yu.V., Nosacheva I.M. Peroxide precursors for the destruction of the carbon chain in the processes of liquid-phase oxidation of saturated compounds at stages following the formation of alcohol and ketone. *Vestnik Kuzbasskogo gosudarstvennogo tekhnicheskogo universiteta = Bulletin of the Kuzbass State Technical University*. 2003;5: 92–103 (in Russ.).
17. Ishii Y. A novel catalysis of *N*-hydroxyphthalimide (NHPI) combined with $Co(acac)_n$ (n = 2 or 3) in the oxidation of organic substrates with molecular oxygen. *J. Mol. Catal. A: Chem*. 1997;117(1–3):123–137. https://doi.org/10.1016/S1381-1169(96)00265-8
18. Dobras G., Orlińska B. Aerobic oxidation of alkylaromatic hydrocarbons to hydroperoxides catalysed by *N*-hydroxyimides in ionic liquids as solvents. *Appl. Catal. A: Gen*. 2018;561: 59–67. https://doi.org/10.1016/j.apcata.2018.05.012

15. Сапунов В.Н., Кошель Г.Н., Румянцева Ю.Б., Курганова Е.А., Кукушкина Н.Д. Роль *N*-гидроксифталимида в механизме реакции жидкофазного окисления *п*-цимола. *Нефтехимия*. 2013;53(3):193–198. https://doi.org/10.7868/S0028242113030106
16. Перкель А.Л., Воронина С.Г., Бунеева Е.И., Непомнящих Ю.В., Носачёва И.М. Пероксидные предшественники деструкции углеродной цепи в процессах жидкофазного окисления насыщенных соединений на стадиях, следующих за образованием спирта и кетона. *Вестник Кузбасского государственного технического университета*. 2003;5:92–103.
17. Ishii Y. A novel catalysis of *N*-hydroxyphthalimide (NHPI) combined with $Co(acac)_n$ (n = 2 or 3) in the oxidation of organic substrates with molecular oxygen. *J. Mol. Catal. A: Chem*. 1997;117(1–3):123–137. https://doi.org/10.1016/S1381-1169(96)00265-8
18. Dobras G., Orlińska B. Aerobic oxidation of alkylaromatic hydrocarbons to hydroperoxides catalysed by *N*-hydroxyimides in ionic liquids as solvents. *Appl. Catal. A: Gen*. 2018;561: 59–67. https://doi.org/10.1016/j.apcata.2018.05.012

About the authors

Valentin N. Sapunov, Dr. Sci. (Chem), Professor, Department of Chemical Technology of Basic Organic and Petrochemical Synthesis, Mendeleev University of Chemical Technology of Russia (9, Miusskaya pl., Moscow, 125047, Russia). sapunovvals@gmail.com. Scopus Author ID 7006540459, RSCI SPIN-code 9357-5030, https://orcid.org/0000-0002-1006-5436

Yuriy L. Zotov, Dr. Sci. (Chem.), Professor, Department of Organic and Petrochemical Synthesis Technology, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: ylzotov@mail.ru. Scopus Author ID 7003371961, RSCI SPIN-code 7543-9740, http://orcid.org/0000-0001-6301-0570

Nguyen Thanh Tung, Engineer, Department of Organic and Petrochemical Synthesis Technology, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: thanhtung92dh@gmail.com. https://orcid.org/0009-0006-7386-8910

Evgeniy V. Shishkin, Dr. Sci. (Chem.), Professor, Department of Organic and Petrochemical Synthesis Technology, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: shishkin@vstu.ru. Scopus Author ID 7004314557, RSCI SPIN-code 3280-1800, https://orcid.org/0000-0002-2994-422X

Yuriy V. Popov, Dr. Sci. (Chem.), Professor, Department of Organic and Petrochemical Synthesis Technology, Volgograd State Technical University (28, pr. im. V.I. Lenina, Volgograd, 400005, Russia). E-mail: iury.popov@yandex.ru. Scopus Author ID 26028090100, RSCI SPIN-code 4582-3342, http://orcid.org/0000-0001-5659-028X

Об авторах

Сапунов Валентин Николаевич, д.х.н., профессор кафедры химической технологии основного органического и нефтехимического синтеза, ФГБОУ ВО «Российский химико-технологический университет им. Д.И. Менделеева» (125047, Россия, Москва, Миусская пл., д. 9). E-mail: sapunovvals@gmail.com. Scopus Author ID 7006540459, SPIN-код РИНЦ 9357-5030, https://orcid.org/0000-0002-1006-5436

Зотов Юрий Львович, д.х.н., профессор кафедры технологии органического и нефтехимического синтеза, ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: ylzotov@mail.ru. Scopus Author ID 7003371961, SPIN-код РИНЦ 7543-9740, http://orcid.org/0000-0001-6301-0570

Нгуен Тхань Тунг, инженер, кафедра технологии органического и нефтехимического синтеза, ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: thanhtung92dh@gmail.com. https://orcid.org/0009-0006-7386-8910

Шишкин Евгений Вениаминович, д.х.н., профессор кафедры технологии органического и нефтехимического синтеза, ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: shishkin@vstu.ru. Scopus Author ID 7004314557, SPIN-код РИНЦ 3280-1800, https://orcid.org/0000-0002-2994-422X

Попов Юрий Васильевич, д.х.н., профессор кафедры технологии органического и нефтехимического синтеза, ФГБОУ ВО «Волгоградский государственный технический университет» (400005, Россия, Волгоград, пр-т им. В.И. Ленина, д. 28). E-mail: iury.popov@yandex.ru. Scopus Author ID 26028090100, SPIN-код РИНЦ 4582-3342, http://orcid.org/0000-0001-5659-028X

Translated from Russian into English by M. Povorin
Edited for English language and spelling by Dr. David Mossop

Tonkie Khimicheskie Tekhnologii = Fine Chemical Technologies.
2024;19(6):508–516
ISSN 2686-7575 (Online)

Biochemistry and biotechnology
Биохимия и биотехнология

UDC 661.723.097.3:546.733
https://doi.org/10.32362/2410-6593-2024-19-6-508-516
EDN BWUXJG

CC BY

RESEARCH ARTICLE

Increasing the efficiency of bioreactor operation for cultivation of methane-oxidizing bacteria under conditions of decreasing carbon dioxide concentration in the cultural liquid

Vladimir M. Kochetkov ✉, **Ivan S. Gaganov, Dmitry V. Tolkin, Vladimir V. Kochetkov, Pavel A. Nyunkov**
Giprobiosintez, Moscow, 119571 Russia
✉ *Corresponding author, e-mail: kwm@bk.ru*

Abstract

Objectives. The work set out to develop a bioreactor that incorporates a carbon dioxide removal unit within the apparatus gas phase, which is capable of operating without the need for supplementary compression apparatus. As part of testing the developed equipment in order to ascertain its capacity for enhanced biomass production, the principal fermentation system parameters that facilitate the optimal bioreactor productivity in conditions of carbon dioxide removal from the apparatus gas phase were identified.

Methods. A series of tests were conducted on the fermentation unit with the objective of controlling the oxygen and carbon dioxide content in the gas phase of the bioreactor. This was achieved using an in-line gas analyzer fitted with electrochemical sensors. The oxygen and carbon dioxide content in the gas phase was determined by means of gas chromatography. The oxygen and natural gas flow rates were determined using a thermal electronic flow controller equipped with thermoresistive elements. The oxygen content of the cultural liquid was determined by means of an optical oxygen sensor with integrated transducer. The pH level in the bioreactor was monitored and maintained using an electrochemical pH sensor.

Results. The efficacy of the newly devised jet-type bioreactor design, which permits the incorporation of a carbon dioxide removal unit into the fermentation system without requiring supplementary compression apparatus, was evaluated through experimentation. The system was tested with the carbon dioxide removal unit included in the design, resulting in a 64% increase in bioreactor productivity and a 18% reduction in oxygen consumption as a component of the gas supply.

Conclusions. The operational parameters of a technological bioreactor that facilitate a stable continuous process of bacterial cultivation were identified.

Keywords

bioreactor, fermenter, fermentation, biomass, protein, carbon dioxide, ejector, methane-oxidizing bacteria, *Methylococcus capsulatus*

Submitted: 22.05.2024
Revised: 25.07.2024
Accepted: 18.10.2024

For citation

Kochetkov V.M., Gaganov I.S., Tolkin D.V., Kochetkov V.V., Nyunkov P.A. Increasing the efficiency of bioreactor operation for cultivation of methane-oxidizing bacteria under conditions of decreasing carbon dioxide concentration in the cultural liquid. *Tonk. Khim. Tekhnol.* = *Fine Chem. Technol*. 2024;19(6):508–516. https://doi.org/10.32362/2410-6593-2024-19-6-508-516

© V.M. Kochetkov, I.S. Gaganov, D.V. Tolkin, V.V. Kochetkov, P.A. Nyunkov, 2024

НАУЧНАЯ СТАТЬЯ

Повышение эффективности работы биореактора для культивирования метанокисляющих бактерий за счет снижения концентрации углекислого газа в культуральной жидкости

В.М. Кочетков ✉, **И.С. Гаганов, Д.В. Толкин, В.В. Кочетков, П.А. Нюньков**

ООО «ГИПРОБИОСИНТЕЗ», Москва, 119571 Россия

✉ *Автор для переписки, e-mail: kwm@bk.ru*

Аннотация

Цели. Разработать конструкцию биореактора, позволяющую включить в свой состав узел удаления углекислого газа из газовой фазы аппарата, функционирующий без использования дополнительного компрессионного оборудования; провести испытания разработанного оборудования с целью увеличения его производительности по биомассе; определить основные параметры работы ферментационной системы, при которых достигается максимальная продуктивность биореактора в условиях извлечения углекислого газа из газовой фазы аппарата.

Методы. Проведена серия испытаний ферментационной установки с осуществлением контроля содержания кислорода и углекислого газа в газовой фазе биореактора поточным газонализатором с электрохимическими сенсорами. Контрольное определение содержания в газовой фазе кислорода и углекислоты проводилось методом газовой хроматографии. Расход газовых компонентов (кислорода и природного газа) измерялся с помощью теплового электронного регулятора расхода с терморезистивными элементами. Содержание растворенного в культуральной жидкости кислорода определялось оптическим датчиком кислорода со встроенным преобразователем. Уровень pH в биореакторе контролировался и поддерживался с помощью электрохимического pH-датчика.

Результаты. Разработан и испытан биореактор струйного типа. За счет использования внутренних рециркуляционных потоков в ферментационную систему интегрирован узел удаления углекислого газа без применения дополнительного компрессионного оборудования. В процессе испытаний системы с включенным в конструкцию узлом извлечения углекислого газа достигнута увеличенная на 64% продуктивность биореактора и снижен на 18% расход кислорода, как компонента газового питания.

Выводы. Определены технологические параметры работы биореактора, при которых проходит стабильный процесс непрерывного культивирования бактерий.

Ключевые слова

биореактор, ферментер, ферментация, биомасса, белок, углекислый газ, эжектор, метанокисляющие бактерии, *Methylococcus capsulatus*

Поступила: 22.05.2024
Доработана: 25.07.2024
Принята в печать: 18.10.2024

Для цитирования

Кочетков В.М., Гаганов И.С., Толкин Д.В., Кочетков В.В., Нюньков П.А. Повышение эффективности работы биореактора для культивирования метанокисляющих бактерий за счет снижения концентрации углекислого газа в культуральной жидкости. *Тонкие химические технологии*. 2024;19(6):508–516. https://doi.org/10.32362/2410-6593-2024-19-6-508-516

INTRODUCTION

The process of obtaining bacterial biomass from natural gas is currently under active consideration by both research organizations that study the properties of methane-oxidizing bacteria and industry technology companies [2–3]. In the context of current trends of establishing Russian protein and vitamin concentrate production facilities, it is necessary to pay particular attention to the hardware design of the process, since this will ultimately determine the scalability boundaries of the process along with desired volumes of feed protein synthesis.

The technological line for the production of protein from natural gas employs a combination of standard and specialized equipment, including centrifugal and dosing pumps, capacitive equipment, and specialized food equipment. The line utilizes centrifugal separators, spray dryers, and high-temperature product processing systems that act as a pasteurizer. However, the most important equipment in the technological chain of bioprotein production is the bioreactor.

The process of cultivating methane-oxidizing bacteria is conducted on a gas substrate, which has considerable influence on the bioreactor design. The primary characteristics of the fermentation equipment designs, along with an overview of the majority of the documented bioreactor models for protein production from natural gas, are presented in [4]. Furthermore, it is essential to address the matter of carbon dioxide present in the gas phase of the fermenter, which is released by methane-oxidizing microorganisms.

The effect of carbon dioxide on bacterial growth has attracted the attention of researchers since the beginning of the 20th century [5]. With the accumulation of material subjected to analysis, two main areas were identified in which this issue became of paramount importance: food preservation and management of microbiological processes [6]. From a practical standpoint, the inhibitory effect of carbon dioxide on bacterial growth is most relevant to the question of food preservation [7]. The scope of challenges confronting researchers was considerably extended with the advancement and intensification of biotechnological procedures. In [8], the issues related to the presence of carbon dioxide in bioreactors are considered from two distinct perspectives: firstly, in terms of its effect on microorganisms, and secondly, in terms of solubility and diffusion in an aqueous medium. In this context, the advancement of fermentation apparatus for technological procedures wherein carbon dioxide is dispersed into the operational volume, which is generated as a consequence of microbial metabolic processes involved in the cultivation of methane-oxidizing bacteria, is a significant undertaking. This is primarily due to the necessity of guaranteeing the solubility of both oxygen-containing and natural gas in the presence of carbon dioxide in the cultural liquid (CL), which is continuously released by bacteria.

Observing that the data on the impact of carbon dioxide on the growth of methanotrophs are inconclusive, V.V. Lalov[1] noted the need for further investigation into the question of whether this component of the gas phase inhibits bacterial culture growth. The most interesting results concerning the effect of limiting and inhibitory concentrations of components of the gas phase and mineral medium on the growth of *Methylococcus capsulatus* are presented in the publication of R.R. Gayazov[2]. The growth of a *Methylococcus capsulatus* methane-oxidizing bacteria culture (strain VSB-874) obtained at the *VNIISINTEZBELOK* Institute (Russia) was shown to be inhibited with an increase in the partial pressure of carbon dioxide in the gas phase of the bioreactor. The publication [9] presents a method for cultivating bacteria of the genus *Methylococcus*, which is of practical importance in studying the effect of carbon dioxide on the growth of microorganisms. The authors propose the use of compression equipment for the removal of a portion of the carbon dioxide from the gas phase of the bioreactor and its partial return to the liquid phase of the apparatus.

The *GIPROBIOSINTEZ* scientific and technical center considered the results of previous studies on the impact of carbon dioxide on methane-oxidizing bacteria. During the commissioning of pilot plants for the production of protein from natural gas, modifications were made to the bioreactor in order to facilitate the return of the carbon dioxide-free components of the gas supply to the process without the use of compression equipment. Furthermore, tests were conducted on the modified apparatus to obtain empirical data regarding the impact of the purification system for the gas phase of the bioreactor on its overall productivity.

EXPERIMENTAL

Schematic diagram of the fermentation unit

In order to demonstrate the technical feasibility of removing carbon dioxide from the gas phase of the bioreactor, a fermentation system is proposed. The details of this system are outlined in the patent [10]. The schematic diagram of the fermentation unit is shown in Figure.

The unit comprises a fermenter (*1*) with a working volume of 15 L, a centrifugal pump (*2*), an ejector (*4*), a tank for CL recovery (*7*) and a carbon dioxide removal unit comprising two adsorbers (*5a*, *5b*). A centrifugal pump installed on the circulation circuit of the bioreactor is used to pump the CL into the ejector. The gas phase emerging from the upper portion of the bioreactor, which is carried along by the process medium (CL), also enters the ejector. The gas–liquid mixture is introduced into the lower section of the bioreactor working volume via the ejector. The primary technical solution of the proposed fermentation system is the installation of a purification system, specifically a carbon dioxide removal unit, on the gas phase outlet line from the bioreactor to the ejector. This system consists of two alternately operating

[1] Lalov V.V. *Analysis and synthesis of energy-technological systems for the production of fodder protein from natural gas.* Diss. Dr. Sci. (Eng.). Moscow, 1991. 416 p. (in Russ.).

[2] Gayazov R.R. *Limitation and inhibition of METHYLOCOCCUS CAPSULATUS growth by components of mineral medium and gas phase.* Diss. Cand. Sci. (Biol.). Russian Academy of Sciences. Institute of Biochemistry and Physiology of Microorganisms. Pushchino, 1992. 127 p. (in Russ.).

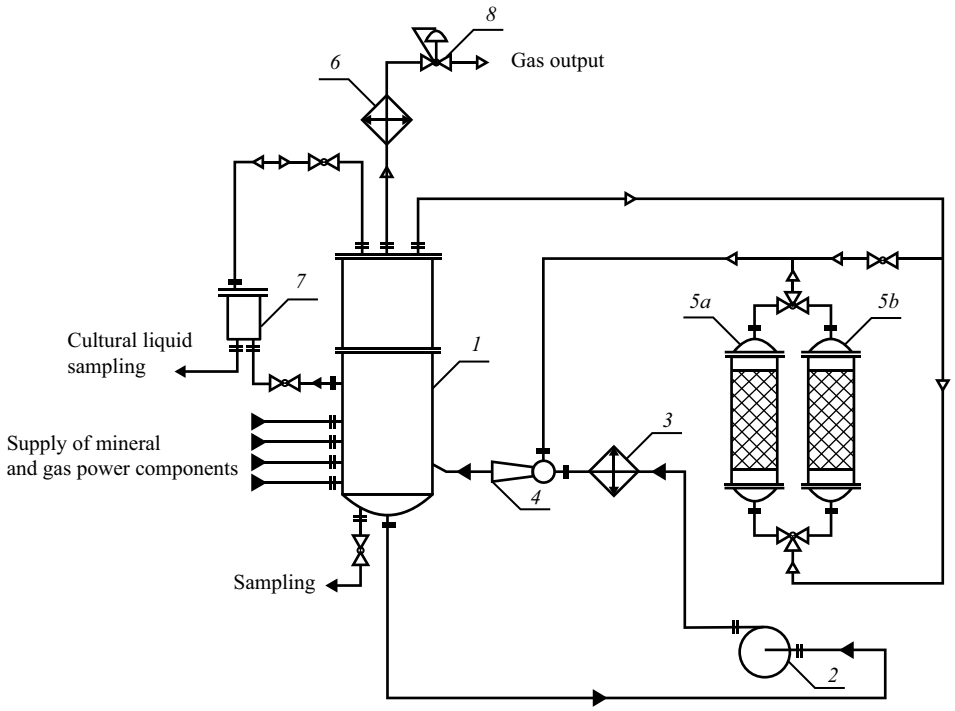


Fig. Modified fermentation unit for methane production from natural gas: (*1*) bioreactor; (*2*) centrifugal pump; (*3*) heat exchanger; (*4*) ejector; (*5a*, *5b*) adsorbers; (*6*) condenser; (*7*) cultural liquid collector; (*8*) upstream pressure regulator [10]

adsorbers. The principal benefit of this configuration is the capacity to link the purification apparatus to the gas recirculation circuit in advance of the pressure jet ejector. This enables the return of the gas phase purified from carbon dioxide to the fermenter without the need for supplementary compression apparatus.

Carbon dioxide removal unit

The gas recirculation line incorporates a bypass line with control valves for ascertaining the ratio of gas directed to the adsorbers for purification to the quantity of gas entering the ejector directly from the fermenter for mixing with the CL. In the carbon dioxide removal unit, which is situated within the fermentation unit and used to separate gases present in the gas phase, a variety of purification techniques may be employed. These include the use of amine solutions for absorption, aqueous potassium carbonate solutions, and membranes for the selective gas separation. In order to exhibit the parametric values of the fermentation process obtained for the modified bioreactor design, a more cost-effective adsorption process is proposed in the purification unit. A group of adsorbents with selective affinity for carbon dioxide was selected based on their absorption capacity at a gas phase pressure in the bioreactor (p_{react}) of 2 barg. Values of carbon dioxide capacity at given pressures and absorption temperature t_{ads} are given in Table 1.

In light of the aforementioned parameters, the adsorbent AMSORB® PLUS was identified as the optimal choice. The composition of the adsorbent is presented in Table 2.

When selecting an adsorbent, it is essential to consider not only the capacity and selectivity of the material in question, but also its chemical composition. The proposed adsorbent comprises components and solutions that are employed as calcium sources and introduced into the bioreactor to facilitate the bacterial cultivation process.

Bioreactor operating modes

In order to evaluate the efficiency of the fermentation system, its operation was tested in two modes: firstly, without a purification system, and secondly, with the use of a carbon dioxide removal unit, which was represented by two adsorbers.

In order to achieve the first mode of operation (Mode No. 1), the gas phase from the bioreactor was fed into the ejector via a bypass line by which means it was mixed with the CL. This bypass line circumvented the adsorbers. The apparatus was supplied with gas supply components: natural gas, oxygen and air in the ratio of 1 : 0.9 : 1. The process gas flow rate was regulated by means of electronic mass flow rate controllers (F-201CV) produced by *Bronkhorst High-Tech* (Netherlands). These controllers comprise a thermal electronic flow rate

Table 1. Absorption capacity of adsorbents

Adsorbent	Manufacturer	t_{ads}, °C	p_{react}, barg	Carbon dioxide (CO_2) capacity, mmol/g (mgCO_2/g)	Reference
Molecular sieve X13	*Zeochem* (Switzerland)	30	2	4.6 (202.4)	[11]
Zeolite NaY	*UOP* (USA)	25	2	5.0 (220.0)	[12]
Activated carbon	*Samchunri* (Korea)	45	2	3.0 (132.0)	[13]
Calcium hydroxide $Ca(OH)_2$	*Aldrich Chemical Company* (USA)	650	–	10.7 (470.8)	[14]
AMSORB® ($Ca(OH)_2$-based)	*Armstrong* (United Kingdom)	36.1	–	4.0 (176.9)	[15]
AMSORB® PLUS	*Armstrong* (United Kingdom)	35–40	–	7.8 (345)	[16], [17]

Table 2. Composition of AMSORB® PLUS adsorbent

Component	Content, wt %
Calcium hydroxide $Ca(OH)_2$	77.0–88.0
Calcium sulfate pentahydrate $CaSO_4 \cdot 5H_2O$	0.6–1.5
Calcium chloride $CaCl_2$	2.0–3.5
Water H_2O	10.0–18.0

controller with thermoresistive elements. The process was conducted at a temperature of 42°C. The bioreactor was provided with a solution of essential mineral nutrients required for optimal culture growth, as well as a continuous flow of ammonia water to maintain a pH range of 5.6–5.8 for CL. The pH in the bioreactor was measured using an EasyFerm Plus ARC 225 electrochemical sensor developed by *Hamilton* (USA). The content of dissolved oxygen in CL was determined using a VisiFerm DO Arc 225 H2 optical oxygen sensor (*Hamilton*, USA). The requisite flow velocity within the apparatus (in excess of 0.25 h^{-1}) was achieved by introducing process water into the apparatus. The reactor was pressurized at 2 barg to ensure that the carbon dioxide content in the circulating gas phase—and, consequently, in dissolved form in the CL—would not lead to disturbance of the cultivation regime by inhibiting the growth of methane-oxidizing bacteria (Footnote 2).

Upon identifying the second operational mode (Mode No. 2) of the fermentation system, the gas phase from the bioreactor was directed to the ejector via the purification unit. The apparatus was provided with the gas supply components comprising natural gas, oxygen and air. The flow rate ratio of the fed components was modified to values of 1.0 : 0.7 : 1.6 throughout the course of the experiment. The reactor is pressurized to 4 barg while maintaining the other process conditions. The carbon dioxide removal unit was constructed in such a way as to regulate the ratio of circulating gas entering directly into the ejector and being subsequently directed to the adsorbers. The control mechanism enables the delivery of a target load (gas flow with CO_2 content) to each operational adsorber, while ensuring that the carbon dioxide content in the gas phase does not exceed the required value for a pre-determined period of adsorber operation. The composition of the gas phase in the bioreactor was monitored using a MAG-6 gas analyzer (Russia, TU 26.51.53-016-70203816-2021[3]) with built-in sensors to determine the volume fraction of oxygen and carbon dioxide. The content of the methane, oxygen and carbon dioxide components was continuously recorded. In accordance with the data given in Gayazov's work (Footnote 2), the volume content of carbon dioxide in the gas phase was selected to be 3% to exclude its inhibiting effect on plant growth at a set apparatus pressure of 4 barg. Chromatography was used to determine the content of the gas phase components. Twice a day, a sample was taken from the gas phase of the bioreactor and analyzed on a chromatograph of the Chromatec-Crystal 5000.2 brand (*Chromatec*, Russia) using a column Mss. 316 2 m × 3 mm NaX 60/80 (*Chromatec*, Russia). Helium was used as a carrier gas; the detector temperature was 180°C; the column temperature was 60/180°C. Each sample was analyzed at least twice.

[3] TU 26.51.53-016-70203816-2021. Description of the measuring instrument type. MAG-6 multicomponent gas analysers. Moscow: Federal Agency for Technical Regulation and Metrology. Order No. 1984 of 10 August 2022.

The carbon dioxide purification unit was commissioned in a working fermentation system at a volume content of carbon dioxide in the gas phase of the bioreactor of 3 vol %. A portion amount of AMSORB® PLUS adsorbent (United Kingdom) was added to two pre-washed and drained adsorbers, one of which had been commissioned. The operating time of the adsorbent placed in the volume of the apparatus was determined by the level of carbon dioxide in the gas phase of the bioreactor. When the carbon dioxide content in the gas phase of the bioreactor rose above 3% by volume, the gas flow was switched to a parallel adsorber filled with a fresh portion of adsorbent. The spent adsorbent was replaced in the adsorber. The adsorber was started up with a new batch of adsorbent according to the work cycle.

RESULTS AND DISCUSSION

The above-described technical solution has been tested and confirmed to work in fermenters that incorporate jet devices as part of their design. The location of the purification unit on the internal gas recirculation line allows the ratio of the amount of gas entering the purifier and via the bypass line directly into the bioreactor to be adjusted using control valves. By means of this control mechanism the purification system can be operated in several bioreactor operating modes characterized by variable values such as the pressure in the apparatus, the composition of the oxygenated gas, and the circulation rate of CL.

According to a comparative analysis of the bioreactor operation modes, the maintenance of consistent performance within the cultivation system is achieved by integrating a gas purification unit into the operational process even with an increase in pressure from 2 to 4 barg.

The parameters of the fermentation system in two comparative modes of operation are presented in Table 3.

As evidenced by the data, the implementation of Mode No. 2 resulted in a notable increase in biomass concentration within the bioreactor, reaching 15.5 g/L at an elevated flow rate from 0.27 to 0.3 h^{-1}. The operation of the fermentation plant in carbon dioxide removal mode allowed the fermentation system's productivity to be increased to a value of 4.6 g/(L·h) (including an increase in system pressure). Accordingly, the enhancement in productivity in comparison to Mode No. 1 reached a level exceeding 64%.

The implementation of Mode No. 2 of operation reduced the oxygen supply to the process by 18% while simultaneously increasing air consumption by 60%. In Mode No. 1, when air flow was provided to the fermenter

Table 3. Fermentation system operation parameters for two modes

Parameter	Mode No. 1 System parameters without using a carbon dioxide removal system (adsorber)	Mode No. 2 System parameters using a carbon dioxide removal system
Input parameters		
Fermenter pressure, barg	2.0	4.0
Air flow rate, nL/h	250	400
Natural gas flow rate (96 vol % methane), nL/h	250	250
Oxygen flow rate (93 vol %), nL/h	220	180
Dilution rate, h^{-1}	0.27	0.3
Output parameters		
The content of oxygen and carbon dioxide in the gas phase, vol % Oxygen Carbon dioxide	 22.7 3.9	 23.2 3.2
Productivity, g/(L·h)	2.8	4.6
Biomass concentration, g/L	10.4	15.5
Dissolved oxygen content, mg/L	1.2	6.6

at a flow rate exceeding 400 nL/h, productivity did not exceed 2.8 g/(L·h).

CONCLUSIONS

The proposed fermentation plant design, which incorporates a carbon dioxide purification unit in the internal circulating gas line, allows the cultivation of methane-oxidizing bacteria with increasing pressure in the bioreactor without the need for additional energy consumption to return purified gas to the system. From the perspective of enhancing the solubility of the gas components of nutrition (methane and oxygen), it is recommended to investigate the impact of elevated pressure within the fermenter on the process productivity. This approach will also optimize the consumption indicators for the gas components of the power supply to ensure a stable process of protein production from natural gas.

The observed increase in the crucial productivity parameter of the bioreactor by over 64% underscores the need to select and implement technological processes that for effectively purifying gas phase from carbon dioxide. The utilization of membranes for selective gas separation in conjunction with the absorption process involving amine solutions represents a promising avenue for investigation in the context of the purification unit.

Authors' contributions

V.M. Kochetkov—research concept, developing the design, scientific editing, formulating the conclusions.

I.S. Gaganov—structural designs, writing the paper, designing the bibliography.

D.V. Tolkin—planning and conducting the experimental work.

V.V. Kochetkov—conducting the experimental work, technical editing, preparing the illustrative materials.

P.A. Nyunkov—systematization of publications, critical analysis.

The authors declare no conflicts of interest.

REFERENCES

1. Oshkin I.Y., Belova S.E., Khokhlachev N.S., *et al*. Molecular Analysis of the Microbial Community Developing in Continuous Culture of *Methylococcus* sp. Concept-8 on Natural Gas. *Microbiology*. 2020;89(5):551–559. https://doi.org/10.1134/S0026261720050173
[Original Russian Text: Oshkin I.Yu., Belova S.E., Khokhlachev N.S., Semenova V.A., Chervyakova O.P., Chernushkin D.V., Tikhonova E.N., Mardanov A.V., Ravin N.V., Popov V.O., Pimenov N.V., Dedysh S.N. Molecular Analysis of the Microbial Community Developing in Continuous Culture of *Methylococcus* sp. Concept-8 on Natural Gas. *Mikrobiologiya*. 2020;89(5):556–565 (in Russ.). https://doi.org/10.31857/S0026365620050171]
2. Chervinskaya A.S, Voropaev V.S., Shmakov E.A., Martynov D.V., Bondarenko P.Y., Bochkov M.A., Portnov S.A., Novikov S.N. *Fermenter and Fermentation Unit for Continuous Cultivation of Microorganisms*. RF Pat. RU 2728193. Publ. 28.07.2020 (in Russ.).
3. Listov E.L., Neboisha Ya. *Apparatus for Growing Microorganisms in Large-Tonnage Production*: RF Pat. RU 2769504. Publ. 01.04.2022 (in Russ.).
4. Kochetkov V.M., Gaganov I.S., Kochetkov V.V., Nyunkov P.A. Technology and implementation of the fermentative unit for bioprotein production from natural gas. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2023;18(3):230–242. https://doi.org/10.32362/2410-6593-2023-18-3-230-242
5. Coyne F.P. The effect of carbon dioxide on bacterial growth. *Proc. R. Soc. Lond. Ser. B.* 1933;113(782):196–217. https://doi.org/10.1098/rspb.1933.0041
6. Dixon N.M., Kell D.B. The inhibition by CO_2 of the same inhibition rate of growth and metabolism of microorganisms. *J. Appl. Bacteriol*. 1989;67(2):109–136. https://doi.org/10.1111/j.1365-2672.1989.tb03387.x
7. Devlieghere F., Debevere J., Van Impe J. Concentration of carbon dioxide in the water phase as a parameter to model the effect of a modified atmosphere on microorganisms. *Int. J. Food Microbiol.* 1998;43(1–2):105–113. https://doi.org/10.1016/s0168-1605(98)00101-9

СПИСОК ЛИТЕРАТУРЫ

1. Ошкин И.Ю., Белова С.Э., Хохлачев Н.С., Семенова В.А., Червякова О.П., Чернушкин Д.В., Тихонова Е.Н., Марданов А.В., Равин Н.В., Попов В.О., Пименов Н.В., Дедыш С.Н. Молекулярный анализ состава микробного сообщества, формирующегося при непрерывном культивировании *Methylococcus* sp. concept-8 на природном газе. *Микробиология*. 2020;89(5):556–565. https://doi.org/10.31857/S0026365620050171
2. Червинская А.С., Воропаев В.С., Шмаков Е.А., Мартынов Д.В., Бондаренко П.Ю., Бочков М.А., Портнов С.А., Новиков С.Н. *Ферментер и ферментационная установка для непрерывного культивирования микроорганизмов*: пат. RU 2728193 РФ. Заявка № 2019118203; заявл. 11.06.2019; опубл. 28.07.2020.
3. Листов Е.Л., Небойша Я. *Аппарат для выращивания микроорганизмов в крупнотоннажном производстве*: пат. RU 2769504 РФ. Заявка № 2021112069; заявл. 27.04.2021; опубл. 01.04.2022.
4. Кочетков В.М., Гаганов И.С., Кочетков В.В., Нюньков П.А. Технологическое и аппаратурное оформление ферментационного узла процесса получения биопротеина из природного газа. *Тонкие химические технологии*. 2023;18(3):230–242. https://doi.org/10.32362/2410-6593-2023-18-3-230-242
5. Coyne F.P. The effect of carbon dioxide on bacterial growth. *Proc. R. Soc. Lond. Ser. B.* 1933;113(782):196–217. https://doi.org/10.1098/rspb.1933.0041
6. Dixon N.M., Kell D.B. The inhibition by CO_2 of the same inhibition rate of growth and metabolism of microorganisms. *J. Appl. Bacteriol*. 1989;67(2):109–136. https://doi.org/10.1111/j.1365-2672.1989.tb03387.x
7. Devlieghere F., Debevere J., Van Impe J. Concentration of carbon dioxide in the water phase as a parameter to model the effect of a modified atmosphere on microorganisms. *Int. J. Food Microbiol.* 1998;43(1–2):105–113. https://doi.org/10.1016/s0168-1605(98)00101-9

8. Ho Ch.S., Smith M.D., Shanahan J.F. Carbon Dioxide Transfer in Biochemical Reactors. *Adv. Biochem. Eng. Biotechnol*. 1987;35:84–124. https://doi.org/10.1007/bfb0004427
9. Shmushkin A.A., Lalov V.V., Grigoryan A.N. *Method for Culturing Microorganisms*: USSR Pat. 811846. Publ. 07.08.1983 (in Russ.).
10. Gaganov I.S., Kochetkov V.M., Nyunkov P.A., Kochetkov V.V. *Fermentation Plant for Cultivation of Methane-Oxidizing Bacteria*: EP Pat. 045062. Publ. 27.10.2023.
11. Siriwardane R.V., Shen M.S., Fisher E.P. Adsorption of CO_2 on Zeolites at Moderate Temperatures. *Energy & Fuels*. 2005;19(3):1153–1159. http://doi.org/10.1021/ef040059h
12. Shi Y., Liu Q., He Y. CO_2 Capture Using Solid Sorbents. In: Chen W.Y., Suzuki T., Lackner M. (Eds.). *Handbook of Climate Change Mitigation and Adaptation*. Springer; 2016. P. 2349–2404. https://doi.org/10.1007/978-3-319-14409-2_83
13. Na B.K., Koo K.K., Eum H.M., Lee H., Song H.K. CO_2 Recovery from Flue Gas by PSA Process using Activated Carbon. *Korean J. Chem. Eng*. 2001;18(2):220–227. http://doi.org/10.1007/BF02698463
14. Wu S.F., Beum T.H., Yang J.I., Kim J.N. Properties of Ca-Base CO_2 Sorbent Using $Ca(OH)_2$ as Precursor. *Ind. Eng. Chem. Res.* 2007;46(24):7896–7899. http://doi.org/10.1021/ie070135e
15. Murray J.M., Renfrew C.W., McCrystal C.B., Jones D.S., Fee H. A New Carbon Dioxide Absorbent for Use in anesthetic breathing systems. *Anesthesiology*. 1999;91(5):1342–1348. https://doi.org/10.1097/00000542-199911000-00026
16. Struys M.M.R.F., Bouche M.P.L.A., Rolly G., Vandevivere Y.D.I., Dyzers D., Goeteyn W., Versichelen L.F.M., Van Bocxlaer J.F.P., Mortier E.P. Production of compound A and carbon monoxide in circle systems: an *in vitro* comparison of two carbon dioxide absorbents. *Anaesthesia*. 2004;59(6):584–589. https://doi.org/10.1111/j.1365-2044.2004.03704.x
17. Kobayashi S., Bito H., Morita K., Katoh T., Sato S. Amsorb Plus and Drägersorb Free, two new-generation carbon dioxide absorbents that produce a low compound A concentration while providing sufficient CO_2 absorption capacity in simulated sevoflurane anesthesia. *J. Anesth*. 2004;18(4):277–281. https://doi.org/10.1007/s00540-004-0253-5

8. Ho Ch.S., Smith M.D., Shanahan J.F. Carbon Dioxide Transfer in Biochemical Reactors. *Adv. Biochem. Eng. Biotechnol*. 1987;35:84–124. https://doi.org/10.1007/bfb0004427
9. Шмушкин А.А., Лалов В.В., Григорян А.Н. *Способ выращивания микроорганизмов*: пат. 811846 СССР. Заявка № 2805913; заявл. 27.07.1979; опубл. 07.08.1983.
10. Гаганов И.С., Кочетков В.М., Нюньков П.А., Кочетков В.В. *Ферментационная установка для культивирования метанокисляющих бактерий*: пат. 045062 ЕП. Заявка № 202390480; заявл. 28.02.2023; опубл. 27.10.2023.
11. Siriwardane R.V., Shen M.S., Fisher E.P. Adsorption of CO_2 on Zeolites at Moderate Temperatures. *Energy & Fuels*. 2005;19(3):1153–1159. http://doi.org/10.1021/ef040059h
12. Shi Y., Liu Q., He Y. CO_2 Capture Using Solid Sorbents. In: Chen W.Y., Suzuki T., Lackner M. (Eds.). *Handbook of Climate Change Mitigation and Adaptation*. Springer; 2016. P. 2349–2404. https://doi.org/10.1007/978-3-319-14409-2_83
13. Na B.K., Koo K.K., Eum H.M., Lee H., Song H.K. CO_2 Recovery from Flue Gas by PSA Process using Activated Carbon. *Korean J. Chem. Eng*. 2001;18(2):220–227. http://doi.org/10.1007/BF02698463
14. Wu S.F., Beum T.H., Yang J.I., Kim J.N. Properties of Ca-Base CO_2 Sorbent Using $Ca(OH)_2$ as Precursor. *Ind. Eng. Chem. Res.* 2007;46(24):7896–7899. http://doi.org/10.1021/ie070135e
15. Murray J.M., Renfrew C.W., McCrystal C.B., Jones D.S., Fee H. A New Carbon Dioxide Absorbent for Use in anesthetic breathing systems. *Anesthesiology*. 1999;91(5):1342–1348. https://doi.org/10.1097/00000542-199911000-00026
16. Struys M.M.R.F., Bouche M.P.L.A., Rolly G., Vandevivere Y.D.I., Dyzers D., Goeteyn W., Versichelen L.F.M., Van Bocxlaer J.F.P., Mortier E.P. Production of compound A and carbon monoxide in circle systems: an *in vitro* comparison of two carbon dioxide absorbents. *Anaesthesia*. 2004;59(6):584–589. https://doi.org/10.1111/j.1365-2044.2004.03704.x
17. Kobayashi S., Bito H., Morita K., Katoh T., Sato S. Amsorb Plus and Drägersorb Free, two new-generation carbon dioxide absorbents that produce a low compound A concentration while providing sufficient CO_2 absorption capacity in simulated sevoflurane anesthesia. *J. Anesth*. 2004;18(4):277–281. https://doi.org/10.1007/s00540-004-0253-5

About the authors

Vladimir M. Kochetkov, Head of the Technological Department, GIPROBIOSINTEZ (10, Testovskaya ul., Moscow, 123112, Russia). E-mail: kwm@bk.ru. Scopus Author ID 58535713700, https://orcid.org/0000-0003-1194-9732

Ivan S. Gaganov, Leading Engineer-Technologist, GIPROBIOSINTEZ (10, Testovskaya ul., Moscow, 123112, Russia). E-mail: ivan.gaganov@yandex.ru. Scopus Author ID 57224575918, https://orcid.org/0000-0003-4837-2332

Dmitry V. Tolkin, Leading Engineer, GIPROBIOSINTEZ (10, Testovskaya ul., Moscow, 123112, Russia). E-mail: tolkin.d@gibios.ru. https://orcid.org/0009-0002-4415-6683

Vladimir V. Kochetkov, Technician-Technologist, GIPROBIOSINTEZ (10, Testovskaya ul., Moscow, 123112, Russia). E-mail: vvkochetkov@bk.ru. Scopus Author ID 59376710800, https://orcid.org/0000-0002-1570-5893

Pavel A. Nynkov, General Manager, GIPROBIOSINTEZ (10, Testovskaya ul., Moscow, 123112, Russia). E-mail: nyunkov.P@gibios.ru. Scopus Author ID 58536061400, https://orcid.org/0000-0002-1232-7460

Об авторах

Кочетков Владимир Михайлович, начальник технологического отдела, ООО «ГИПРОБИОСИНТЕЗ» (123112, Россия, Москва, ул. Тестовская, д. 10). E-mail: kwm@bk.ru. Scopus Author ID 58535713700, https://orcid.org/0000-0003-1194-9732

Гаганов Иван Сергеевич, ведущий инженер-технолог, ООО «ГИПРОБИОСИНТЕЗ» (123112, Россия, Москва, ул. Тестовская, д. 10). E-mail: ivan.gaganov@yandex.ru. Scopus Author ID 57224575918, https://orcid.org/0000-0003-4837-2332

Толкин Дмитрий Владимирович, ведущий инженер, ООО «ГИПРОБИОСИНТЕЗ» (123112, Россия, Москва, ул. Тестовская, д. 10). E-mail: tolkin.d@gibios.ru. https://orcid.org/0009-0002-4415-6683

Кочетков Владимир Владимирович, техник-технолог, ООО «ГИПРОБИОСИНТЕЗ» (123112, Россия, Москва, ул. Тестовская, д. 10). E-mail: vvkochetkov@bk.ru. Scopus Author ID 59376710800, https://orcid.org/0000-0002-1570-5893

Нюньков Павел Андреевич, генеральный директор ООО «ГИПРОБИОСИНТЕЗ» (123112, Россия, Москва, ул. Тестовская, д. 10). E-mail: nyunkov.P@gibios.ru. Scopus Author ID 58536061400, https://orcid.org/0000-0002-1232-7460

Translated from Russian into English by N. Isaeva
Edited for English language and spelling by Thomas A. Beavitt

Tonkie Khimicheskie Tekhnologii = Fine Chemical Technologies.
2024;19(6):517–527
ISSN 2686-7575 (Online)

Synthesis and processing of polymers and polymeric composites
Синтез и переработка полимеров и композитов на их основе

UDC 617-089.844+544.03
https://doi.org/10.32362/2410-6593-2024-19-6-517-527
EDN ZWXRLX

CC BY

RESEARCH ARTICLE

Influence of modifying additives on the structure and properties of biodegradable mixtures based on poly-3-hydroxybutyrate and nitrile butadiene rubber

Pavel A. Povernov[1], Lyudmila S. Shibryaeva[1, 2, ✉], Sergei M. Anshin[3]

[1] *N.M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, 119334 Russia*

[2] *MIREA — Russian Technological University, Moscow, 119454 Russia*

[3] *Plekhanov Russian University of Economics, Moscow, 117997 Russia*

✉ *Corresponding author, e-mail: lyudmila.shibryaeva@yandex.ru*

Abstract

Objectives. To investigate polymer composite materials based on poly-3-hydroxybutyrate (PHB) of microbiological origin and the synthetic nitrile butadiene rubber NBR-28. The biodegradability of PHB implies the possibility of its use for invasive medical purposes; however, this is significantly limited by its brittleness. The aim of this work was to search for approaches to altering the molecular structure of PHB-based composites, in order to impart them with sufficient physical and mechanical characteristics and increase their compatibility without violating biodegradability.

Methods. Reaction mixtures contained the elastic material NBR-28, various modifiers (sorbitan oleate, epoxidized soybean oil, siloxane rubber), and additional polymer components (ethylene–vinyl acetate copolymer and polybutylene adipate terephthalate). The mixtures were prepared in a PL 2200-3 plasticorder (*Brabender*, Russia) by pressing, holding the material at 180°C under pressure for 3 min followed by quenching in cold water. The surfaces of the films and plates of the mixtures were studied using an Axio Imager Z2m optical microscope (*Carl Zeiss*, Germany) with the Axio Vision software at 50× and 200× magnification in reflected light. The mechanical properties of materials under tension were measured using an Instron 3365 universal tensile testing machine (*Instron*, United Kingdom).

Results. The role of modifiers and polymer additives in the PHB–NBR-28 composites and their influence on the morphology of mixtures, crystallinity, and mechanical characteristics were established. The introduction of modifiers made it possible to reduce the average particle size of the NBR-28 phase in the PHB matrix by 30–50%, additionally changing their morphology. In this case, the uniformity of particle distribution increased, having a positive effect on the mechanical characteristics of the systems.

Conclusions. It was shown that the modifiers change the morphology of mixtures, reduce the average particle size of the NBR phase by 30–50%, and positively affect the strength of the systems. Owing to changes in the structure of their interfacial layers and, as a consequence, physical and mechanical characteristics, the resulting composites render suitable for use in reparative bone and dental surgery, as well as for creating wound healing materials.

Keywords

polyhydroxyalkanoates, bone implants, osteogenesis, biodegradable polymer composite materials, osteoplastic materials

Submitted: 06.04.2023
Revised: 17.09.2024
Accepted: 16.10.2024

© P.A. Povernov, L.S. Shibryaeva, S.M. Anshin, 2024

For citation

Povernov P.A., Shibryaeva L.S., Anshin S.M. Influence of modifying additives on the structure and properties of biodegradable mixtures based on poly-3-hydroxybutyrate and nitrile butadiene rubber. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2024;19(6):517–527. https://doi.org/10.32362/2410-6593-2024-19-6-517-527

НАУЧНАЯ СТАТЬЯ

Влияние модифицирующих добавок на структуру и свойства биоразлагаемых смесей на основе поли-3-гидроксибутирата и бутадиен-нитрильного каучука

П.А. Повернов[1], Л.С. Шибряева[1, 2, ✉], С.М. Аншин[3]

[1] *Институт биохимической физики им. Н.М. Эмануэля, Российская академия наук, Москва, 119334 Россия*

[2] *МИРЭА — Российский технологический университет, Москва, 119454 Россия*

[3] *Российский экономический университет им. Г.В. Плеханова, Москва, 117997 Россия*

✉ *Автор для переписки, e-mail: lyudmila.shibryaeva@yandex.ru*

Аннотация

Цели. Изготовить и исследовать полимерные смесевые материалы на основе поли-3-гидроксибутирата (ПГБ) микробиологического происхождения и синтетического бутадиен-нитрильного каучука (БНКС) марки БНКС-28. Биоразлагаемость ПГБ предполагает возможность его применения в инвазивных медицинских целях, однако это в значительной степени ограничивается его хрупкостью. В связи с этим, целью данной работы являлось нахождение способов изменения молекулярной структуры композитов на основе ПГБ для придания им достаточных физико-механических характеристик и увеличения их совместимости без нарушения биоразлагаемости.

Методы. В работе использовался эластичный материал БНКС-28, а также различные модификаторы (сорбитан олеат, эпоксидированное соевое масло, силоксановый каучук) и дополнительные полимерные компоненты: сополимер этилена и винилацетата и полибутиленадипинаттерефталат. Смеси были получены в пластикордере PL 2200-3 (*Брабендер*, Россия). Пленки смесей готовили прессованием, выдерживая материал при 180°C под давлением в течение 3 мин с последующей закалкой в холодной воде. Поверхности пленок и пластин смесей изучали с помощью оптического микроскопа Axio Imager Z2m (*Carl Zeiss*, Германия) с программным обеспечением Axio Vision при увеличении 50× и 200× в отраженном свете. Упруго-прочностные свойства материалов при растяжении измерялись на универсальной разрывной машине Instron 3365 (*Instron*, Великобритания).

Результаты. Установлена роль модификаторов и полимерных добавок в композиции ПГБ–БНКС и их влияние на морфологию, кристалличность и механические характеристики смесей. Введение модификаторов позволило снизить средний размер частиц фазы БНКС в матрице ПГБ на 30–50%, а также изменило их морфологию. Равномерность распределения частиц при этом увеличилась, что позитивно повлияло на механические характеристики систем.

Выводы. Показано, что модификаторы меняют морфологию смесей, уменьшают средний размер частиц фазы БНКС на 30–50% и положительно влияют на прочность систем. Полученные композиции ввиду изменения структуры их межфазных слоев и, как следствие, физико-механических характеристик пригодны для применения в репаративной костной и зубной хирургии, а также для создания ранозаживляющих материалов.

Ключевые слова

полигидроксиалканоаты, костные имплантаты, остеогенез, биодеградируемые полимерные композиционные материалы, остеопластические материалы

Поступила: 06.04.2023
Доработана: 17.09.2024
Принята в печать: 16.10.2024

Для цитирования

Повернов П.А., Шибряева Л.С., Аншин С.М. Влияние модифицирующих добавок на структуру и свойства биоразлагаемых смесей на основе поли-3-гидроксибутирата и бутадиен-нитрильного каучука. *Тонкие химические технологии*. 2024;19(6):517–527. https://doi.org/10.32362/2410-6593-2024-19-6-517-527

INTRODUCTION

Currently, great importance is attached to the research and development of materials with applications in medicine, in particular, in osteoplasty and dental implant surgery [1–5]. An active search is underway for materials and composites which would have an osteoplastic effect while at the same time be resistant to bacteria [6–8]. However, due to their high degree of biodegradability, polymeric materials suitable for this application have a number of disadvantages in physical and mechanical characteristics and thus require modification.

The literature describes some possible variants of modification of polymers, such as hydrophilization of the polymer surface by plasma-chemical treatment in order to increase adhesive properties [9], or modification by introducing a mineral component, nanosized hydroxyapatite, in order to form porous calcium phosphate composites with a controlled structure [10]. In addition, research is underway to synthesize modifiers specifically for biodegradable polymers based on polyester polyols, and surfactants with a hyperbranched structure [11, 12]. Furthermore, research is being conducted to create fibrous materials from poly-3-hydroxybutyrate (PHB) with modifiers based on metal complexes with tetraphenylporphyrin [13, 14].

This paper examines the modification of PHB by introducing nitrile butadiene rubber and various compatibilizers and elasticizers in its composition with the purpose of improving the compatibility of the composite, its adhesion and strength, while maintaining the required degree of biodegradability.

EXPERIMENTAL

The main polymer under study was PHB synthesized by the microbiological method (*Biomer*, Germany) with a molecular weight of $2.1 \cdot 10^5$ and a crystallinity of 65%. Elasticity to the composite was imparted by adding NBR-28 AMN nitrile butadiene rubber (*SK Sibur*, Russia), a synthetic polymer, a product of the radical copolymerization of butadiene with acrylonitrile in an aqueous emulsion.

The following components were used as modifiers and compatibilizers.

1. Epoxidized soybean oil (ESO) (*Novokhim*, Russia) acts as a plasticizer and a heat and light stabilizer. The use of ESO is to increase the flexibility of the finished product without changing its chemical properties, reduce the melting point, and improve its heat and light stability [15].
2. Ethylene–vinyl acetate copolymer (EVA) (*Rusplast*, Russia). The addition of EVA increases the elasticity of the polymer composite material by 15–25% and improves the physical and mechanical properties. EVA helps to reduce the interfacial tension between the components and increase the thermodynamic compatibility of the polymer and rubber [16]. It is likely that the introduction of a hydroxyl-functionalized EVA copolymer (EVA-F) may further improve the interaction of the components thanks to hydrogen bonds between the terminal hydroxyl groups of PHB and EVA-F. Functionalization can be carried out by alkaline alcoholysis of EVA-F in a 30% KOH solution [17, 18].
3. Siloxane rubber (*Ekotek*, Russia) is an inert elastomer which does not affect biological processes and is suitable for use in medical implants. It is a biocompatible, hypoallergenic, chemically stable component, and can be used as a compatibilizer for the mixture during plasticization.
4. Polybutylene adipate terephthalate (PBAT) (*Anhui Juhong Trading Co.*, China) is a random polymer with a disordered structure that cannot crystallize. Therefore, this polymer can impart such characteristics to the composite as high flexibility, high impact toughness, low stiffness, and low elastic modulus, as well as a wide range of melting temperatures. It is important to note that this is a completely biodegradable polymer [19].
5. Oleic acid polyethylene glycol ester PEG-7 (*PCC Exol SA*, Poland) can serve as a compatibilizer for PHB and NBR-28. This is due to good compatibility with both components according to literature data [20]. At the same time, PEG-7 is a biodegradable substance, soluble both in water and in most organic solvents, allowing it to be used in the preparation of composite materials using both high-temperature and solution technologies. PEG-7 is safe and approved for indirect contact with food products and medicines.

Samples of the original polymers and mixtures containing 10, 20, 30, 40, 50, 60, 70, 80, and 90 wt % NBR-28 in PHB were studied. In addition, we also examined three-component mixtures based on PHB and NBR-28 with the addition of modifiers (ESO, EVA, siloxane rubber, oleic acid ester) or additional polymers (EVA and PBAT).

The composites were produced in a PL 2200-3 plasticorder (*Brabender*, Russia), which models a closed-type rubber mixer. This device provides a wide range of temperatures and operating speeds, allowing the composites to be studied over a wide range of shear rates. Mixing of the composites for this work was performed for 5 min at a temperature of 160 to 180°C, depending on the ratio of components and the type of modifier.

For samples with increased rubber content, the mixing of PHB and NBR-28 was also carried out on

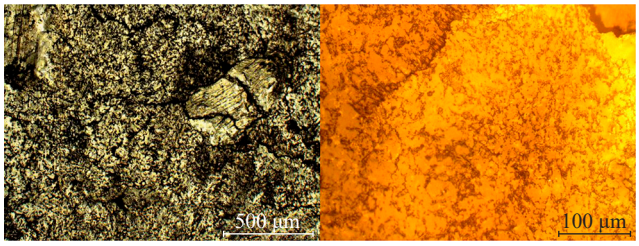
PD-240 laboratory rollers (*GDW*, Germany) with heating to 60°C, preliminary plasticization of rubber for 10 min, and subsequent introduction of a PHB powder.

Films of the mixtures were prepared by pressing on a laboratory press. The material was maintained at 180°C under pressure for 3 min with subsequent quenching in cold water. The surfaces of the films and plates of the mixtures were studied with an Axio Imager Z2m optical microscope (*Carl Zeiss*, Germany) with Axio Vision software at 50× and 200× magnification in reflected light.

RESULTS AND DISCUSSION

Figures 1–6 show macrophotographs of various three-component mixtures with modifiers at 50× and 200× magnification.

An analysis of the macrophotographs of these samples determined that siloxane rubber (Fig. 1) significantly affected the size distribution of NBR-28 particles in the PHB phase. The large particle size adversely affected the uniformity of particle distribution and can cause the sample properties to vary with the thickness of the product and the degree of its unevenness, as well as could increase the brittleness of the composite because of the presence of large foreign particles in the matrix, which serve as centers for the growth of defects and cracks in the sample.

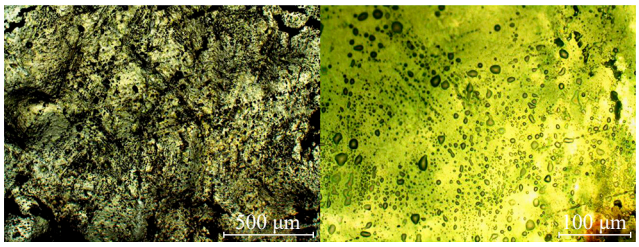


(a) (b)

Fig. 1. PHB–NBR-28 + siloxane rubber (90/10% + 3%) at (a) 50× and (b) 200× magnification

The microphotographs at 200× magnification show that, although the morphology of these mixtures is heterogeneous, the NBR-28 particles (dark inclusions in the matrix) are finely dispersed fibrous aggregates which form bundles and ribbons, in contrast to spherical aggregates in the case of the PHB–NBR-28 mixture without the use of a compatibilizer [21]. The particle size in the two-component mixture is 60–100 μm, whereas the length of the NBR-28 bundles using a compatibilizing agent reaches 20–40 μm.

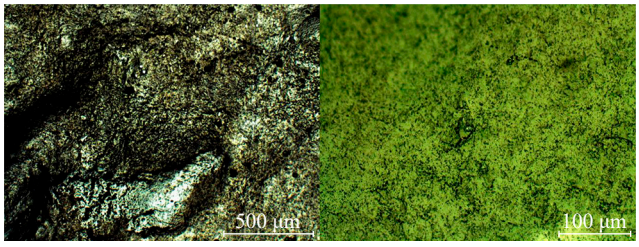
In order to increase the elasticity and biodegradability of the mixtures, the possibility of using PBAT as a component to replace rubber was explored. As can be seen in Fig. 2, mixing of PBAT and PHB in the presence of small amounts of ESO can give uniformly distributed dispersed PBAT particles in the PHB matrix. In this work, drop-shaped PBAT inclusions with sizes from 10 to 30 μm were obtained. At the same time, due to the high biodegradability of both components [19, 22], the ratios of the components can be varied over a wide range. This allows the parameters of the decomposition rate and the mechanical characteristics of the polymer composite material for the required medical application to be varied (dental implant, bone implant for low or high mechanical load, biodegradable suture material, etc.).



(a) (b)

Fig. 2. PHB–PBAT + ESO (70/30% + 3%) at (a) 50× and (b) 200× magnification

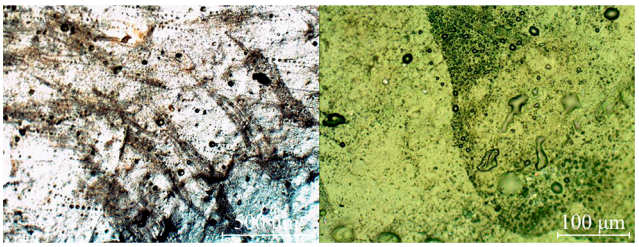
An interesting composite to study was the three-component mixture PHB–NBR-28–PBAT with a low rubber content and PHB as the main matrix-forming component (Fig. 3). In this case, since the compatibilization of both PHB with PBAT and NBR with PBAT was quite successful, PBAT served as a compatibility agent for the other two components. Based on the micrographs, in the case of three components, both PBAT and NBR were uniformly distributed both in the PHB matrix as a whole and relative to each other. The sizes of NBR and PBAT particles in the matrix were even smaller than in the case of siloxane rubber and ESO. The thickness of the aggregates did not exceed 20 μm, and the length was <40 μm. The average calculated equivalent diameter of such particles was 125 μm.



(a) (b)

Fig. 3. PHB–NBR-28–PBAT (60/10/30%) at (a) 50× and (b) 200× magnification

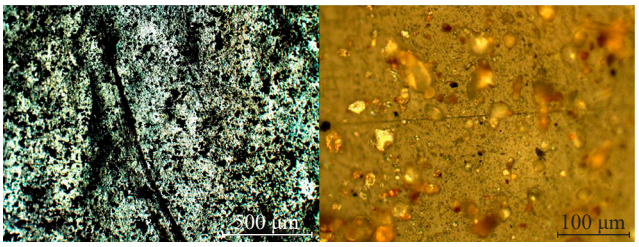
The combination of PHB and NBR-28 with EVA also proved to be relatively successful (Fig. 4), but the question of the biodegradation of these composites in dynamics remained open.



(a) (b)

Fig. 4. PHB–NBR-28–EVA (60/10/30%) at (a) 50× and (b) 200× magnification

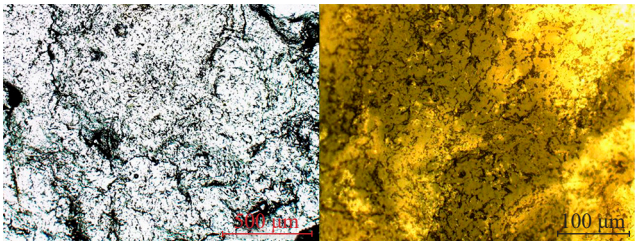
Figure 5 presents the micrographs of the sample containing 30 wt % EVA after biodegradation in soil for 1 month. It can be seen that volume defects and cavities in the structure of the material formed during this time. However, it is currently unknown whether all components decompose in this mixture or the main mass loss occurs due to the destruction of PHB. At present, studies are being conducted on the biodegradation of composites with EVA. They preliminarily show that, at a sufficient degree of biodegradability of these composites, the use of EVA improves the thermodynamic compatibility of the polymer matrix and rubber and reduces the interfacial tension between them.



(a) (b)

Fig. 5. PHB–NBR-28–EVA (60/10/30%) after biodegradation in soil for 1 month at (a) 50× and (b) 200× magnification

The introduction of PEG-7 as a compatibilizer (Fig. 6), as in the case of siloxane rubber and ESO, produced the expected effect of dispersing the components in each other and facilitated the processing of the composite in the plasticorder.



(a) (b)

Fig. 6. PHB–NBR-28 + PEG-7 (90/10% + 3%) at (a) 50× and (b) 200× magnification

The effect of additives taken in small amounts (up to 3%) on the crystalline and amorphous regions and the degree of crystallinity of the composite was studied by means of X-ray fluorescence analysis of the samples (Figs. 7a–7c) with the same content of NBR-28. A statistical analysis showed that the average calculated degrees of crystallinity of the samples with siloxane rubber and PEG-7 additives were 54% and 56%, respectively, whereas the degree of crystallinity of the composite without a modifier was 61%. We believe that the decrease in the size of inclusions of the NBR-28 phase upon the introduction of a modifier gives rise to strong interphase interactions. Modifiers behave as crystallization nuclei. The growth of small crystallites increases segmental mobility. This leads to an increase in the free volume, the porosity, and the number of physical entanglements.

In pure PHB without either additives or rubber, the degree of crystallinity was 70%. The lowest degree of crystallinity for the PHB–NBR-28 composite was observed at an equimass ratio of the components of 36% (Fig. 7d). This indicates that the addition of NBR-28 to PHB changes the phase and molecular structure by the intermolecular interaction of the components. In any further study of these composites, it is advisable to apply methods for studying the free surface energy and other surface properties of polymer composite materials, e.g., the methods used to study the effect of additives on the surface properties of NBR-based composites described previously [23, 24].

The main problem of the PHB biopolymer is its high brittleness, rendering it impossible to use it in pure form for any biomedical purposes [25]. In the case of the two-component system PHB–NBR, a large amount of rubber in the system (from 30%) significantly increases the elasticity of the system, although sharply reducing its ability to biodegrade and the rate of decomposition. Previous studies have confirmed that the content of NBR-28 in the polymer matrix up to 20% leaves the possibility for biodegradation of the polymer in biological environments at a sufficient rate for the growth of cells and vessels in the polymer matrix. It also enables complete decomposition before the onset of complications caused by the rejection of a foreign body by the organism [26]. Therefore, composites with a content of NBR-28 up to 20% will meet a set of requirements for biodegradable medical devices, provided that they are sufficiently elastic. The introduction of modifiers in this case helps to increase the strength characteristics due to better compatibility of components and dispersion of phase particles in the matrix. In addition, modifiers change the microstructure of the composites and can accelerate the processes of polymer biodegradation.

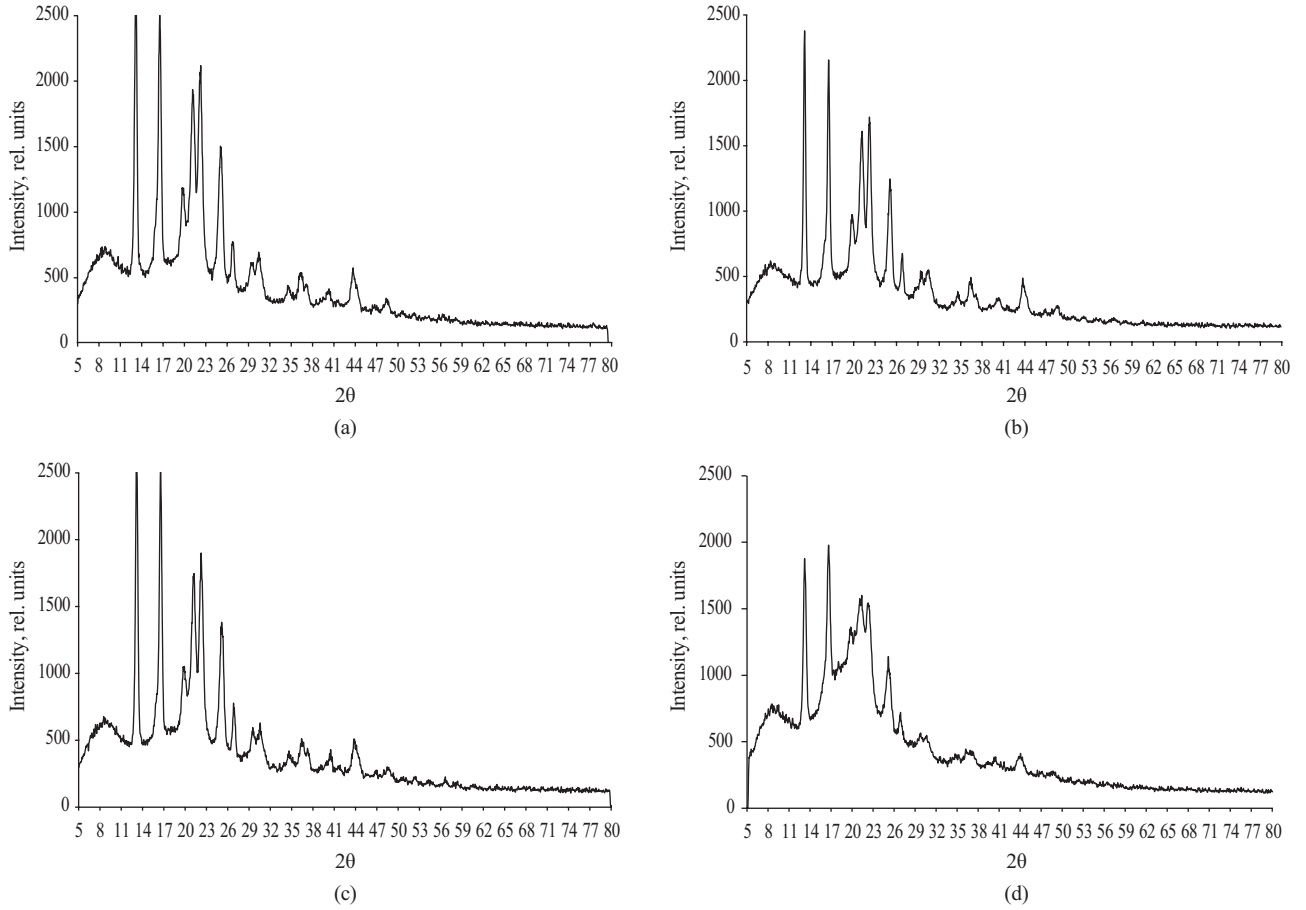


Fig. 7. X-ray fluorescence spectra of the 90% PHB–10% NBR-28 composite (a) without the addition of a compatibilizer, (b) with the addition of 3% siloxane rubber, and (c) with the addition of 3% PEG-7; (d) X-ray fluorescence spectrum of the 50% PHB–50% NBR-28 composite without a modifier

Tests used to determine the elastic strength properties under tension (GOST 270-75[1]) were carried out on an Instron 3365 universal tensile testing machine (*Instron*, United Kingdom). Of the composites studied, pronounced elastic properties were demonstrated by all PHB–NBR-28 two-component composites with a rubber content of 30% and higher, the PHB–NBR-28–EVA (60/10/30%) composite, and, to a lesser extent, the PHB–NBR-28–PBAT (60/10/30%) composite. Some samples modified only with compatibilizing additives (ESO, siloxane rubber), 90% PHB contents, and up to 10% NBR-28 proved to be brittle for testing of this kind. Clearly the strengthening of the composite, as expected, can be carried out in two ways: by increasing the content of NBR-28 to more than 20% in the presence of a compatibilizer; or by introducing an elastic polymer as an additional component, as in the case of the PHB–NBR-28–PBAT and PHB–NBR-28–EVA systems. The following table presents the obtained mechanical characteristics of these composites.

Note that composite 6 (PHB–NBR-28, 10/90%) is not biodegradable to a sufficient degree and serves only for comparative analysis, as does composite 5 with a NBR-28 content of 50%. In turn, sample 4 with a content of NBR-28 of 30% is borderline suitable for certain medical products. However, the degree of its biodegradability and the possibility of enhancing degradation with additives have yet to be studied.

Composites with introduced EVA and PBAT showed a tensile strength exceeding the strength of composites 3 and 4 with a high rubber content without additional additives. Meanwhile, based on the data of reviews [25, 27] concerning methods of strengthening composites with PHB, the comparative strength of the PHB–NBR-28 and PHB–NBR-28–EVA composites is somewhat higher than those of PHB composites with starch, cellulose, and polymer fillers (ethylene–vinyl

[1] GOST 270-75. Interstate Standard. Rubber. Method of the determination elastic and tensile stress-strain properties. Moscow: Standartinform; 2008.

Table. Mechanical characteristics of polymer composites

No.	Composite	Elongation at break, %	Tensile strength, MPa
1	PHB–NBR-28 (90/10%)	0–2 (brittle fracture)	16 ± 1
2	PHB–NBR-28–PBAT (60/10/30%)	21 ± 1	32 ± 1.5
3	PHB–NBR-28–EVA (60/10/30%)	26 ± 1.5	37 ± 2
4	PHB–NBR-28 (70/30%)	33 ± 2	33 ±1.5
5	PHB–NBR-28 (50/50%)	58 ± 3	48 ± 2.5
6	PHB–NBR-28 (10/90%)	85 ± 4	61.5 ± 3

acetate copolymer, polylactide). However, it is lower than those of fibers obtained from mixtures of PHB and ultrahigh-molecular-weight PHB by cold drawing [28] or fibers of a PHB copolymer with poly-3-hydroxyhexanoate [29].

The process of complete degradation of three-component composites with EVA and PBAT is currently being studied. According to the results of biodegradation for 100 days in the soil, preliminary conclusions can be made about a gradual decrease in the weight of samples and a significant degree of crack growth up to 40 and 70 nm thick in the case of EVA and PBAT, respectively. It can also be assumed that the weight loss of the composite during degradation in the case of EVA and PBAT is equal to or even exceeds the weight loss of the PHB–NBR-28 composites without additional additives.

CONCLUSIONS

In this work, the optimal mode of mixing of the PHB–NBR-28–modifier composite was selected. The necessary modifiers were found to improve the compatibility of the components and impart the necessary physical and mechanical properties while maintaining the required degree of biodegradability.

A more extended study into the biodegradability of the components is being conducted elsewhere; however, preliminary findings indicate a sufficient degree of biodegradability of the most promising composites, namely, PHB–NBR-28–EVA (60/10/30%) and PHB–NBR-28–PBAT (60/10/30%). With regard to composites with 90% PHB, 10% NBR-28, and an additive (ESO, siloxane rubber), the modifier in an amount of 1–3% does not adversely affect their biodegradability. A composite with pure PHB and NBR-28 in a ratio of 9 : 1 has already been studied earlier and is suitable for use in biodegradable medical products.

As expected, the introduction of modifiers, allowed the average particle size of the NBR phase in the PHB matrix to be reduced by 30–50% or greater. It also changed their morphology from spherical particles of 60–100 nm to elongated fibers aggregated into bundles and ribbons with a thickness of 5 to 20 nm and a length of 10 to 50 nm for different modifiers. The uniformity of particle distribution increased, beneficially affecting the mechanical characteristics of the systems. However, without the introduction of the second polymer (EVA or PBAT), the brittleness of the systems remained quite high; therefore, modifiers (ESO, siloxane rubber) will be of interest for use at an increased NBR content (presumably 20% or more).

Authors' contributions

L.S. Shibryaeva—concept and management of the work, editing the text of the article.

P.A. Povernov—conducting experiments, discussing the results of the study, and writing the text of the article.

S.M. Anshin—conducting experiments, discussing the results of the study.

The authors declare no conflicts of interest.

REFERENCES

1. Verma M.L., Kumar S., Jeslin J., Dubey N.K. Microbial Production of Biopolymers with Potential Biotechnological Applications. In: *Biopolymer-Based Formulations*. Elsevier; 2020. P. 105–137. https://doi.org/10.1016/B978-0-12-816897-4.00005-9
2. Rebelo R., Vila N., Rana S., Fangueiro R. Poly Lactic Acid Fibre Based Biodegradable Stents and Their Functionalization Techniques. In: Fangueiro R., Rana S. (Eds.). *Natural Fibres: Advances in Science and Technology Towards Industrial Applications*. *RILEM Bookseries*. 2017;12:331–342. https://doi.org/10.1007/978-94-017-7515-1_25
3. Vasilyev I.Yu., Ananyev V.V., Kolpakova V.V., Sardzhveladze A.S. Development of technology for producing biodegradable hybrid composites based on polyethylene, starch, and monoglycerides. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2020;15(6):44–55. https://doi.org/10.32362/2410-6593-2020-15-6-44-55
4. Vasilyev I.Yu., Ananyev V.V., Chernov M.E. Biodegradable packaging materials based on low density polyethylene, starch and monoglycerides. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2022;17(3):231–241. https://doi.org/10.32362/2410-6593-2022-17-3-231-241
5. Gomzyak V.I., Demina V.A., Razuvaeva E.V., Sedush N.G., Chvalun S.N. Biodegradable polymer materials for medical applications: From implants to organs. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2017;12(5):5–20 (in Russ.). https://doi.org/10.32362/2410-6593-2017-12-5-5-20
6. Lykoshin D.D., Zaitsev V.V., Kostromina M.A., Esipov R.S. New-generation osteoplastic materials based on biological and synthetic matrices. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2021;16(1):36–54. https://doi.org/10.32362/2410-6593-2021-16-1-36-54
7. Gomzyak V.I., Puchkov A.A., Artamonova N.E., Polyakov D.K., Simakova G.A., Gritskova I.A., Chvalun S.N. Physico-chemical properties of biodegradable hyperbranched polyester polyol based on 2,2-bis(methylol)propionic acid. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2018;13(4):67–73 (in Russ.). https://doi.org/10.32362/2410-6593-2018-13-4-67-73
8. Gordienko M.G., Somov T.N., Yusupova Y.S., Chupikova N.I., Menshutina N.V. Preparation of spherical microparticles from biodegradable natural and synthetic polymers for their application in regenerative medicine. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2015;10(5):66–76 (in Russ.).
9. Luque-Agudo V., Hierro-Oliva M., Gallardo-Moreno A.M., González-Martín M.L. Effect of plasma treatment on the surface properties of polylactic acid films. *Polym. Test*. 2021;96:107097. https://doi.org/10.1016/j.polymertesting.2021.107097
10. Gorshenyov V.N., Ziangirova M.Yu., Kolesov V.V., Krasnopol'skaya L.M., Prosvirin A.A., Teleshev A.T. New additive technologies for forming complex bone structures for medical and biological applications. *RENSIT*. 2019;11(3):369–390 (in Russ). https://doi.org/10.17725/rensit.2019.11.369
11. Gomzyak V.I., Artamonova N.E., Kovtun I.D., Kamyshinsky R.A., Gritskova I.A., Chvalun S.N. Heterophase Polymerization of Styrene in the Presence of Boltorn Polyester Polyol. *Polym. Sci. Ser. B*. 2020;62(1):22–29. https://doi.org/10.1134/S156009041905004X
12. Sedush N.G., Kadina Yu.A., Razuvaeva E.V., *et al.* Nanoformulations of Drugs Based on Biodegradable Lactide Copolymers with Various Molecular Structures and Architectures. *Nanotechnol. Rep*. 2021;16(4):421–438. https://doi.org/10.1134/S2635167621040121

СПИСОК ЛИТЕРАТУРЫ

1. Verma M.L., Kumar S., Jeslin J., Dubey N.K. Microbial Production of Biopolymers with Potential Biotechnological Applications. In: *Biopolymer-Based Formulations*. Elsevier; 2020. P. 105–137. https://doi.org/10.1016/B978-0-12-816897-4.00005-9
2. Rebelo R., Vila N., Rana S., Fangueiro R. Poly Lactic Acid Fibre Based Biodegradable Stents and Their Functionalization Techniques. In: Fangueiro R., Rana S. (Eds.). *Natural Fibres: Advances in Science and Technology Towards Industrial Applications*. *RILEM Bookseries*. 2017;12:331–342. https://doi.org/10.1007/978-94-017-7515-1_25
3. Васильев И.Ю., Ананьев В.В., Колпакова В.В., Сарджвеладзе А.С. Разработка технологии получения биоразлагаемых композиций на основе полиэтилена, крахмала и моноглицеридов. *Тонкие химические технологии*. 2020;15(6):44–55. https://doi.org/10.32362/2410-6593-2020-15-6-44-55
4. Васильев И.Ю., Ананьев В.В., Чернов М.Е. Биоразлагаемые упаковочные материалы на основе полиэтилена низкой плотности, крахмала и моноглицеридов. *Тонкие химические технологии*. 2022;17(3):231–241. https://doi.org/10.32362/2410-6593-2022-17-3-231-241
5. Гомзяк В.И., Демина В.А., Разуваева Е.В., Седуш Н.Г., Чвалун С.Н. Биоразлагаемые полимерные материалы для медицины: от импланта к органу. *Тонкие химические технологии*. 2017;12(5):5–20. https://doi.org/10.32362/2410-6593-2017-12-5-5-20
6. Лыкошин Д.Д., Зайцев В.В., Костромина М.А., Есипов Р.С. Остеопластические материалы нового поколения на основе биологических и синтетических матриксов. *Тонкие химические технологии*. 2021;16(1):36–54. https://doi.org/10.32362/2410-6593-2021-16-1-36-54
7. Гомзяк В.И., Пучков А.А., Артамонова Н.Е., Поляков Д.К., Симакова Г.А., Грицкова И.А., Чвалун С.Н. Физико-химические свойства биоразлагаемого сверхразветвленного полиэфирполиола на основе 2,2-бис(метилол)пропионовой кислоты. *Тонкие химические технологии*. 2018;13(4):67–73. https://doi.org/10.32362/2410-6593-2018-13-4-67-73
8. Гордиенко М.Г., Сомов Т.Н., Юсупова Ю.С., Чупикова Н.И., Меньшутина Н.В. Получение микрочастиц из биодеградируемых природных и синтетических полимеров для применения их в области регенеративной медицины. *Тонкие химические технологии*. 2015;10(5):66–76.
9. Luque-Agudo V., Hierro-Oliva M., Gallardo-Moreno A.M., González-Martín M.L. Effect of plasma treatment on the surface properties of polylactic acid films. *Polym. Test*. 2021;96:107097. https://doi.org/10.1016/j.polymertesting.2021.107097
10. Горшенёв В.Н., Зиангирова М.Ю., Колесов В.В., Краснопольская Л.М., Просвирин А.А., Телешев А.Т. Новые аддитивные технологии формирования сложных костных структур для медико-биологических применений. *РЭНСИТ*. 2019;11(3):369–390. https://doi.org/10.17725/rensit.2019.11.369
11. Gomzyak V.I., Artamonova N.E., Kovtun I.D., Kamyshinsky R.A., Gritskova I.A., Chvalun S.N. Heterophase Polymerization of Styrene in the Presence of Boltorn Polyester Polyol. *Polym. Sci. Ser. B*. 2020;62(1):22–29. https://doi.org/10.1134/S156009041905004X
12. Седуш Н.Г., Кадина Ю.А., Разуваева Е.В., Пучков А.А., Широкова Е.М., Гомзяк В.И., Калинин К.Т., Кулебякина А.И., Чвалун С.Н. Наносомальные лекарственные формы на основе биоразлагаемых сополимеров лактида с различной молекулярной структурой и архитектурой. *Российские нанотехнологии*. 2021;16(4):462–481. https://doi.org/10.1134/S1992722321040117

[Original Russian Text: Sedush N.G., Kadina Yu.A., Razuvaeva E.V., Puchkov A.A., Shirokova E.M., Gomzyak V.I., Kalinin K.T., Kulebyakina A.I., Chvalun S.N. Nanosomal dosage forms based on biodegradable lactide copolymers with different molecular structure and architecture. *Rossiiskie Nanotekhnologii*. 2021;16(4):462–481 (in Russ.). https://doi.org/10.1134/S1992722321040117]

13. Karpova S.G., Ol'khov A.A., Krivandin A.V., *et al.* Effect of zinc–porphyrin complex on the structure and properties of poly(3-hydroxybutyrate) ultrathin fibers. *Polym. Sci. Ser. A.* 2019;61(1):70–84. https://doi.org/10.1134/S0965545X19010140
[Original Russian Text: Karpova S.G., Ol'khov A.A., Krivandin A.V., Shatalova O.V., Popov A.A., Lobanov A.V., Iordanskii A.L. Effect of zinc–porphyrin complex on the structure and properties of poly(3-hydroxybutyrate) ultrathin fibers. *Vysokomolekulyarnye Soedineniya. Seriya A*. 2019;61(1):67–81 (in Russ.). https://doi.org/10.1134/S2308112019010164]
14. Karpova S.G., Ol'khov A.A., Zhul'kina A.L., *et al*. Nonwoven Materials Based on Electrospun Ultrathin Fibers of Poly(3-hydroxybutyrate) and Complex Tin Chloride–Porphyrin. *Polym. Sci. Ser. A.* 2021;63(4):369–381. https://doi.org/10.1134/S0965545X21040040
[Original Russian Text: Karpova S.G., Ol'khov A.A., Zhul'kina A.L., Popov A.A., Iordanskii A.L. Nonwoven Materials Based on Electrospun Ultrathin Fibers of Poly(3-hydroxybutyrate) and Complex Tin Chloride–Porphyrin. *Vysokomolekulyarnye Soedineniya. Seriya A*. 2021;63(4):249–262 (in Russ.). https://doi.org/10.31857/S2308112021040040]
15. Pour-Esmaeil S., Sharifi-Sanjani N., Khoee S., Taheri-Qazvini N. Biocompatible chemical network of *α*-cellulose-ESBO (epoxidized soybean oil) scaffold for tissue engineering application. *Carbohydr. Polym*. 2020;241:116322. https://doi.org/10.1016/j.carbpol.2020.116322
16. Zhang H.-C., Huang J., Zhao P.-F., Lu X. Bio-based ethylene-co-vinyl acetate/poly (lactic acid) thermoplastic vulcanizates with enhanced mechanical strength and shape memory behavior. *Polym. Test*. 2020;87:106537. https://doi.org/10.1016/j.polymertesting.2020.106537
17. Emmanuelle M., Yves C., Nathalie I., Franck E., Laurent G., Philippe F. The Controlled Solvolysis of Ethylene−Vinyl Acetate Copolymers. *Macromolecules*. 2001;34(17):5838–5847. https://doi.org/10.1021/ma0102666
18. Sukhikh E.S., Silant'eva M.E., Lirova B.I., Suvorov A.L., Nadol'skii A.L., Tyukova I.S., Suvorova A.I. Synthesis of copolymers of ethylene and vinyl alcohol (EVA), their structure and membrane properties. In: *Problems of Theoretical and Experimental Chemistry:* Abstracts of reports of the 20th Russian Youth Scientific Conference. Yekaterinburg: 2010. P. 406–408 (in Russ.).
19. Zhang J., Hirschberg V., Rodrigue D. Mechanical fatigue of biodegradable polymers: A study on polylactic acid (PLA), polybutylene succinate (PBS) and polybutylene adipate terephthalate (PBAT). *Int. J. Fatigue*. 2022;159(2):106798. https://doi.org/10.1016/j.ijfatigue.2022.106798
20. Povernov P.A., Shibryaeva L.S., Lyusova L.R., *et al.* The Influence of Mixing Conditions on the Morphology of Poly-3-hydroxybutyrate and Nitrile-Butadiene Rubber Polymer Compositions. *Polym. Sci. Ser. D.* 2022;15(4):628–632. https://doi.org/10.1134/S1995421222040220
21. Zhorina L.A., Rogovina S.Z., Prut E.V., *et al*. Biodegradable compositions based on poly-(3-hydroxybutyrate) and polylactide polyesters obtained from vegetable raw materials. *Polym. Sci. Ser. A.* 2020;62(4):361–367. https://doi.org/10.1134/S0965545X20040136
13. Карпова С.Г., Ольхов А.А., Кривандин А.В., Шаталова О.В., Лобанов А.В., Попов А.А., Иорданский А.Л. Влияние комплекса цинк–порфирин на структуру и свойства ультратонких волокон поли(3-гидроксибутирата). *Высокомолекул. соединения. Сер. А.* 2019;61(1):67–81. https://doi.org/10.1134/S2308112019010164
14. Карпова С.Г., Ольхов А.А., Жулькина А.Л., Попов А.А., Иорданский А.Л. Нетканые материалы на основе ультратонких волокон поли(3-гидроксибутирата) с комплексом хлорид олова–порфирин, полученных электроформованием. *Высокомолекул. соединения. Сер. А.* 2021;63(4):249–262. https://doi.org/10.31857/S2308112021040040
15. Pour-Esmaeil S., Sharifi-Sanjani N., Khoee S., Taheri-Qazvini N. Biocompatible chemical network of *α*-cellulose-ESBO (epoxidized soybean oil) scaffold for tissue engineering application. *Carbohydr. Polym*. 2020;241:116322. https://doi.org/10.1016/j.carbpol.2020.116322
16. Zhang H.-C., Huang J., Zhao P.-F., Lu X. Bio-based ethylene-co-vinyl acetate/poly (lactic acid) thermoplastic vulcanizates with enhanced mechanical strength and shape memory behavior. *Polym. Test*. 2020;87:106537. https://doi.org/10.1016/j.polymertesting.2020.106537
17. Emmanuelle M., Yves C., Nathalie I., Franck E., Laurent G., Philippe F. The Controlled Solvolysis of Ethylene−Vinyl Acetate Copolymers. *Macromolecules*. 2001;34(17):5838–5847. https://doi.org/10.1021/ma0102666
18. Сухих Е.С., Силантьева М.Э., Лирова Б.И., Суворов А.Л., Надольский А.Л., Тюкова И.С., Суворова А.И. Синтез сополимеров этилена и винилового спирта (ЭВС), их структура и мембранные свойства. В сб.: *Проблемы теоретической и экспериментальной химии:* тезисы докладов XX Российской молодежной научной конференции. Екатеринбург. 2010. С. 406–408.
19. Zhang J., Hirschberg V., Rodrigue D. Mechanical fatigue of biodegradable polymers: A study on polylactic acid (PLA), polybutylene succinate (PBS) and polybutylene adipate terephthalate (PBAT). *Int. J. Fatigue*. 2022;159(2):106798. https://doi.org/10.1016/j.ijfatigue.2022.106798
20. Povernov P.A., Shibryaeva L.S., Lyusova L.R., *et al.* The Influence of Mixing Conditions on the Morphology of Poly-3-hydroxybutyrate and Nitrile-Butadiene Rubber Polymer Compositions. *Polym. Sci. Ser. D.* 2022;15(4):628–632. https://doi.org/10.1134/S1995421222040220
21. Жорина Л.А., Роговина С.З., Прут Э.В., Кузнецова О.П., Грачев А.В., Иванушкина Н.Е., Иорданский А.Л., Берлин А.А. Биоразлагаемые композиции на основе полиэфиров поли-(3-гидроксибутирата) и полилактида, получаемых из растительного сырья. *Высокомолекул. соединения. Сер. А.* 2020;62(4):263–270. https://doi.org/10.31857/S2308112020040136
22. Тарасенко А.Д., Дулина О.А., Буканов А.М. Влияние неполимерных компонентов резиновой смеси на поверхностные свойства эластомерных композиций. *Тонкие химические технологии*. 2018;13(5):67–72. https://doi.org/10.32362/2410-6593-2018-13-5-67-72
23. Дулина О.А., Еськова Е.В., Тарасенко А.Д., Котова С.В. Влияние различных факторов на поверхностные свойства эластомерных материалов на основе бутадиен-нитрильных каучуков. *Тонкие химические технологии*. 2022;17(2):152–163. https://doi.org/10.32362/2410-6593-2022-17-2-152-163
24. Yeo J.C.C., Muiruri J.K., Thitsartarn W., Li Z., He C. Recent advances in the development of biodegradable PHB-based toughening materials: Approaches, advantages and applications. *Mater. Sci. Eng.: C*. 2017;92:1092–1116. https://doi.org/10.1016/j.msec.2017.11.006

[Original Russian Text: Zhorina L.A., Rogovina S.Z., Prut E.V., Kuznetsova O.P., Grachev A.V., Ivanushkina N.E., Iordanskii A.L., Berlin A.A. Biodegradable compositions based on poly-(3-hydroxybutyrate) and polylactide polyesters obtained from vegetable raw materials. *Vysokomolekulyarnye Soedineniya. Seriya A*. 2020;62(4):263–270 (in Russ.). https://doi.org/10.31857/S2308112020040136]
22. Tarasenko A.D., Dulina O.A., Bukanov A.M. The effect of non-polymeric components of a rubber mixture on surface properties of elastomer compositions. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2018;13(5):67–72 (in Russ.). https://doi.org/10.32362/2410-6593-2018-13-5-67-72
23. Dulina O.A., Eskova E.V., Tarasenko A.D., Kotova S.V. Influence of various factors on surface properties of elastomeric materials based on nitrile butadiene rubbers. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2022;17(2):152–163. https://doi.org/10.32362/2410-6593-2022-17-2-152-163
24. Yeo J.C.C., Muiruri J.K., Thitsartarn W., Li Z., He C. Recent advances in the development of biodegradable PHB-based toughening materials: Approaches, advantages and applications. *Mater. Sci. Eng.: C*. 2017;92:1092–1116. https://doi.org/10.1016/j.msec.2017.11.006
25. Povernov P.A., Shibryaeva L.S. Scientific approaches to the development of materials based on compositions of poly-3-hydroxybutyrate and polylactide for bone implants. In: *Innovatsii v sozdanii materialov i metodov dlya sovremennoi meditsiny* (*Innovations in the Creation of Materials and Methods for Modern Medicine*): Proceedings of the regional conference. 2020. P. 173–179 (in Russ.).
26. Povernov P.A., Shibryaeva L.S., Lusova L.R., Popov A.A. Modern polymer composite materials for bone surgery: Problems and prospects. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2022;17(6):514–536. https://doi.org/10.32362/2410-6593-2022-17-6-514-536
27. Kabe T., Tsuge T., Kasuya K., Takemura A., Hikima T., Takata M., Iwata T. Physical and Structural Effects of Adding Ultrahigh-Molecular-Weight Poly[(*R*)-3-hydroxybutyrate] to Wild-Type Poly[(*R*)-3-hydroxybutyrate]. *Macromolecules*. 2012;45(4):1858–1865. https://doi.org/10.1021/ma202285c
28. Kabe T., Hongo C., Tanaka T., Hikima T., Takata M., Iwata T. High tensile strength fiber of poly[(*R*)-3-hydroxybutyrate-*co*-(*R*)-3-hydroxyhexanoate] processed by two-step drawing with intermediate annealing. *J. Appl. Polym. Sci*. 2014;132(2):41258. https://doi.org/10.1002/app.41258
25. Повернов П.А., Шибряева Л.С. Научные подходы к разработке материалов на основе композиций из поли-3-гидроксибутирата и полилактида для костных имплантатов. *Инновации в создании материалов и методов для современной медицины:* материалы региональной конференции. 2020. С. 173–179.
26. Повернов П.А., Шибряева Л.С., Люсова Л.Р., Попов А.А. Современные полимерные композиционные материалы для костной хирургии: проблемы и перспективы. *Тонкие химические технологии*. 2022;17(6):514–536. https://doi.org/10.32362/2410-6593-2022-17-6-514-536
27. Kabe T., Tsuge T., Kasuya K., Takemura A., Hikima T., Takata M., Iwata T. Physical and Structural Effects of Adding Ultrahigh-Molecular-Weight Poly[(*R*)-3-hydroxybutyrate] to Wild-Type Poly[(*R*)-3-hydroxybutyrate]. *Macromolecules*. 2012;45(4):1858–1865. https://doi.org/10.1021/ma202285c
28. Kabe T., Hongo C., Tanaka T., Hikima T., Takata M., Iwata T. High tensile strength fiber of poly[(*R*)-3-hydroxybutyrate-*co*-(*R*)-3-hydroxyhexanoate] processed by two-step drawing with intermediate annealing. *J. Appl. Polym. Sci*. 2014;132(2):41258. https://doi.org/10.1002/app.41258

About the authors

Pavel A. Povernov, Postgraduate Student, Junior Researcher, Laboratory of Physico-Chemistry of Compositions of Synthetic and Natural Polymers, N.M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences (4, Kosygina ul., Moscow, 119334, Russia). E-mail: pav3444@yandex.ru. Scopus Author ID 57210264564, ResearcherID ABC-5732-2021, RSCI SPIN-code 1408-2867, https://orcid.org/0000-0003-3017-4397

Lyudmila S. Shibryaeva, Dr. Sci. (Chem.), Professor, Leading Researcher, Laboratory of Physico-Chemistry of Compositions of Synthetic and Natural Polymers, N.M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences (4, Kosygina ul., Moscow, 119334, Russia); Professor, F.F. Koshelev Department of Chemistry and Technology of Processing of Elastomers, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (78, Vernadskogo pr., Moscow, 119454, Russia). E-mail: lyudmila.shibryaeva@yandex.ru. Scopus Author ID 7003539026, ResearcherID A-7634-2014, RSCI SPIN-code 3664-7997, https://orcid.org/0000-0001-6805-4492

Sergey M. Anshin, Junior Researcher, Department of Chemistry of Innovative Materials and Technologies, Plekhanov Russian University of Economics (36, Stremyannyi per., Moscow, 115054, Russia). E-mail: asm51@bk.ru

Об авторах

Повернов Павел Алексеевич, аспирант, младший научный сотрудник, лаборатория физико-химии композиций природных и синтетических полимеров, ФГБУН Институт биохимической физики им. Н.М. Эмануэля, Российская академия наук (199334, Россия, Москва, ул. Косыгина, д. 4). E-mail: pav3444@yandex.ru. Scopus Author ID 57210264564, ResearcherID ABC-5732-2021, SPIN-код РИНЦ 1408-2867, https://orcid.org/0000-0003-3017-4397

Шибряева Людмила Сергеевна, д.х.н., профессор, ведущий научный сотрудник, лаборатория физико-химии композиций природных и синтетических полимеров, ФГБУН Институт биохимической физики им. Н.М. Эмануэля, Российская академия наук (199334, Россия, Москва, ул. Косыгина, д. 4); профессор, кафедра химии и технологии переработки эластомеров им. Ф.Ф. Кошелева, Институт тонких химических технологий им. М.В. Ломоносова, ФГБОУ ВО «МИРЭА – Российский технологический университет» (119454, Россия, Москва, пр-т Вернадского, д. 78). E-mail: lyudmila.shibryaeva@yandex.ru. Scopus Author ID 7003539026, ResearcherID A-7634-2014, SPIN-код РИНЦ 3664-7997, https://orcid.org/0000-0001-6805-4492

Аншин Сергей Михайлович, младший научный сотрудник, кафедра химии инновационных материалов и технологий, ФГБОУ ВО «Российский экономический университет им. Г.В. Плеханова» (115054, Россия, Москва, Стремянный переулок, д. 36). E-mail: asm51@bk.ru

Translated from Russian into English by V. Glyanchenko
Edited for English language and spelling by Dr. David Mossop

Tonkie Khimicheskie Tekhnologii = Fine Chemical Technologies.
2024;19(6):528–535
ISSN 2686-7575 (Online)

Synthesis and processing of polymers and polymeric composites
Синтез и переработка полимеров и композитов на их основе

UDC 678
https://doi.org/10.32362/2410-6593-2024-19-6-528-535
EDN UMETEK

CC BY

RESEARCH ARTICLE

Oscillation rheometry of curing process of epoxy binders modified with polyetherimide

Stepan V. Polunin[1], ✉, Kirill A. Atamas[1], Irina Yu. Gorbunova[1], Polina A. Morozova[1], Konstantin M. Marakhovsky[2]

[1] *Mendeleev University of Chemical Technology of Russia, Moscow, 125047 Russia*

[2] *MIPP – NPO "Plastik," Moscow, 121059 Russia*

✉ *Corresponding author, e-mail: mcnion@gmail.com*

Abstract

Objectives. The aim of this study is to ascertain the influence of polyetherimide on the curing process of epoxy binders.

Methods. The storage modulus and loss modulus of epoxyamine systems were measured as a function of curing time on the Anton Paar MCR 302 rheometer. The experiments were carried out at an oscillation frequency of 1 Hz, with an amplitude aligned with the linear viscoelasticity region, and across a range of temperatures (160, 170, and 180°C). The crossover point was determined when the components of the complex modulus of elasticity are equal according to the obtained dependencies.

Results. The influence of polyetherimide on the curing process of epoxyamine binders was investigated at a thermoplastic content of 5 to 20 pts. wt at three temperatures. In a system modified with 20 pts. wt of polyetherimide, phase separation was observed during the curing process. In systems modified with 10 and 20 pts. wt of polyetherimide, the limiting value of the modulus of elasticity was observed to be higher at 170°C than at 180°C.

Conclusions. The modification of epoxyamine binders with thermoplastic in an amount of 5–20 pts. wt has been observed to extend the time required to reach the crossover point. Furthermore, the curing process markedly slows down in the system comprising 10 pts. wt of thermoplastic content, in which it takes the longest time to reach the crossover point at all three experimental temperatures.

Keywords

oscillation rheometry, crossover point, epoxy oligomer, polyetherimide, phase separation

Submitted: 15.07.2024
Revised: 10.09.2024
Accepted: 18.10.2024

For citation

Polunin S.V., Atamas K.A., Gorbunova I.Yu., Morozova P.A., Marakhovsky K.M. Oscillation rheometry of curing process of epoxy binders modified with polyetherimide. *Tonk. Khim. Tekhnol. = Fine Chem. Technol*. 2024;19(6):528–535. https://doi.org/10.32362/2410-6593-2024-19-6-528-535

© S.V. Polunin, K.A. Atamas, I.Yu. Gorbunova, P.A. Morozova, K.M. Marakhovsky, 2024

НАУЧНАЯ СТАТЬЯ

Осцилляционная реометрия процесса отверждения эпоксидных связующих, модифицированных полиэфиримидом

С.В. Полунин[1], ✉, К.А. Атамас[1], И.Ю. Горбунова[1], П.А. Морозова[1], К.М. Мараховский[2]

[1] *Российский химико-технологический университет им. Д.И. Менделеева, Москва, 125047 Россия*

[2] *Межотраслевой институт переработки пластмасс – НПО «Пластик», Москва, 121059 Россия*

✉ *Автор для переписки, e-mail: mcnion@gmail.com*

Аннотация

Цели. Определение влияния полиэфиримида на процесс отверждения эпоксидных связующих.

Методы. Методом осцилляционной реометрии фиксировали зависимость модуля накопления и модуля потерь эпоксиаминных систем от времени отверждения на приборе MCR 302 фирмы Anton Paar с частотой колебаний 1 Гц и амплитудой, соответствующей области линейной вязкоупругости, при трех температурах 160, 170 и 180°С. По полученным зависимостям определяли точку кроссовера при равенстве составляющих комплексного модуля упругости.

Результаты. Установлено влияние полиэфиримида на процесс отверждения эпоксиаминных связующих при содержании термопласта от 5 до 20 мас. ч. на 100 мас. ч. эпоксидного олигомера при трех температурах. Для системы, модифицированной 20 мас. ч. полиэфиримида, зафиксировано фазовое разделение в процессе сшивания. В системах, содержащих 10 и 20 мас. ч. полиэфиримида, предельное значение модуля упругости оказывается выше при 170°С, чем при 180°С.

Выводы. Введение полиэфиримида в эпоксиаминные связующие в количестве 5–20 мас. ч. увеличивает время достижения точки кроссовера. При этом наиболее сильно замедляется процесс отверждения для системы, содержащей 10 мас. ч. термопласта, время достижения точки кроссовера которой оказывается наибольшим при всех трех температурах эксперимента.

Ключевые слова

осцилляционная реометрия, точка кроссовера, эпоксидный олигомер, полиэфиримид, разделение фаз

Поступила: 15.07.2024
Доработана: 10.09.2024
Принята в печать: 18.10.2024

Для цитирования

Полунин С.В., Атамас К.А., Горбунова И.Ю., Морозова П.А., Мараховский К.М. Осцилляционная реометрия процесса отверждения эпоксидных связующих, модифицированных полиэфиримидом. *Тонкие химические технологии*. 2024;19(6):528–535. https://doi.org/10.32362/2410-6593-2024-19-6-528-535

INTRODUCTION

Epoxy resins are used as binders in reinforced plastics in many industries. The advantages of this class of compounds include good adhesion, high dielectric properties, low curing shrinkage, and excellent chemical resistance [1]. The use of hot curing hardeners enables the attainment of relatively high heat resistance in epoxy polymers. However, deficiencies exhibited in such materials in terms of crack resistance and impact strength limit the range of their potential application.

The resistance of epoxy polymers to brittle fracture can be improved by modifying them with thermoplastics [2–4]. In comparison to the utilization of rubbers and active diluents, this approach offers the distinct advantage of maintaining the glass transition temperature of the cured epoxy oligomer at its original level [5, 6].

In the majority of cases, the initially compatible system of epoxy oligomer and thermoplastic undergoes phase decomposition during the curing process. This is due to the increase in molecular weight of the cured polymer, which in turn contributes to the enhancement of the physical and mechanical properties of the material [7]. Different types of structures are formed in the cured polymers [8]. In [9], examples of extended structures with direct and inverse “matrix–dispersion”, in which the dispersion medium is reactoplastic and thermoplastic, respectively, are demonstrated.

The incorporation of thermoplastics into epoxy oligomers markedly alters their intrinsic characteristics, including viscosity. Consequently, it is of considerable scientific interest to examine the curing process of systems modified in this way. Rotation or oscillation rheometry can be used to measure viscosity and determine gelation time [10]. During the latter,

the dependencies of two components of the complex modulus (|G*|): the storage modulus G′ and the loss modulus G″ on time are recorded. The moment of intersection of the values of these parameters, referred to as the crossover point, is associated in the literature with gel formation in the system [11]. In epoxy binders modified with thermoplastics, the release of the phase enriched in the more viscous component occurs prior to gelation. Consequently, through the utilization of rotation or oscillation rheometry, it is occasionally feasible to ascertain the precise moment of phase separation. This is evidenced by the emergence of distinctive discontinuities in the relationships between shear viscosity or loss modulus and curing time [12].

Previously, the curing process of epoxy oligomer modified with cardo polysulfone copolymer PSFF-70K was investigated by rotational rheometry in constant shear mode [13]. For the system containing 10 pts. wt of thermoplastic content, there is a slight decrease in shear viscosity at the 30th minute at an experimental temperature of 180°C, indicating phase separation during the structuring process. Interestingly, for the binder modified with 5 pts. wt PSFF-70K the longest gelation time was recorded compared to the unmodified binder, which can probably be attributed to the fact that at this content of modifier there is no phase separation of the mixture.

The modification of epoxy oligomer with polyetherimide (PEI) was also studied in [14]. On the infrared spectra of the cured epoxyamine polymer containing 2 wt % of PEI, the authors observed a shift towards lower wave numbers of the peak characteristic of the hydroxyl group, which is also contained in the initial epoxy A type oligomer and is formed after the reaction of the epoxide cycle with the amino group. This can probably be explained by the occurrence of hydrogen bonds between the hydroxyl groups of the epoxy polymer and the imide groups of PEI.

The objective of this work is to study the curing process of PEI-modified epoxyamine binders.

MATERIALS AND METHODS

The binders were prepared on the basis of epoxy oligomer ED-20 (GOST 10587-84[1], *Ya.M. Sverdlov Plant*, Russia). Ultem 1010 grade PEI (*Sabic*, USA) was used as a thermoplastic modifier, which was added to ED-20 at 160°C in an amount of 5, 10, 15, and 20 pts. wt per 100 pts. wt of epoxy oligomer and stirred using a top-drive stirrer until homogeneous solutions were obtained at 160–180°C. 4,4’-diaminodiphenylsulfone was used as a hardener for the binders; this is not indicated in the captions. The hardener was mixed for 30 min at 120°C in an amount of 30 pts. wt per 100 pts. wt of ED-20, which is close to the stoichiometric ratio.

Oscillation rheometry was performed in a plane-to-plane measuring system with a working gap of 1 mm on an MCR 302 rheometer manufactured by *Anton Paar* (Austria) at an oscillation frequency ω = 1 Hz and an amplitude corresponding to the linear viscoelasticity region. The experiments were conducted at three distinct temperatures: 160, 170, and 180°C. Prior to the experiment, the binders were preheated to 130°C in the thermal cabinet, then transferred to the lower fixed plane of the instrument. Next, the gap was set up and the binders were heated to the measurement temperature. During the experiments, the dependencies of the accumulation modulus G′ and loss modulus G″ on the curing time were recorded.

RESULTS AND DISCUSSION

Earlier studies have shown that the epoxy-PEI system is compatible prior to the curing process and characterized by an upper critical solution temperature of 40°C. The initial viscosity of PEI-modified epoxies was also found to be between 2 and 6 kPa·s at room temperature (20°C) [15].

Figure 1 shows the dependencies of the storage modulus and loss modulus on the curing time of epoxyamine binders in semi-logarithmic coordinates at three temperatures.

At the initial stage of the curing process, the loss modulus G″ appears to be higher than the storage modulus G′, which is due to the inability of liquids to store energy under mechanical loading. However, during the curing process, the components of the complex modulus of elasticity increase. At a certain moment at which G′ turns out to be higher than G″, the system under study acquires the characteristics of a solid state. This point in time is called the crossover point (G′ = G″) and is associated with gel formation. The crossover point corresponds to the moment of appearance of a continuous grid of chemical bonds that are formed during the curing process. The time to reach the crossover point is about 18–33 min longer in epoxy binders with thermoplastic modifiers as compared to unmodified ED-20. This is probably due to the slowing down of the curing process, i.e., slowing down of the formation of the chemical bonding network in the epoxyamine binder in the presence of PEI, since the thermoplastic dilutes the reactive system and increases its viscosity as correlated with the literature

[1] GOST 10587-84. State Standard of the USSR. Uncured epoxy resins. Specifications. Moscow: USSR State Committee for Product Quality Management and Standards; 1985.

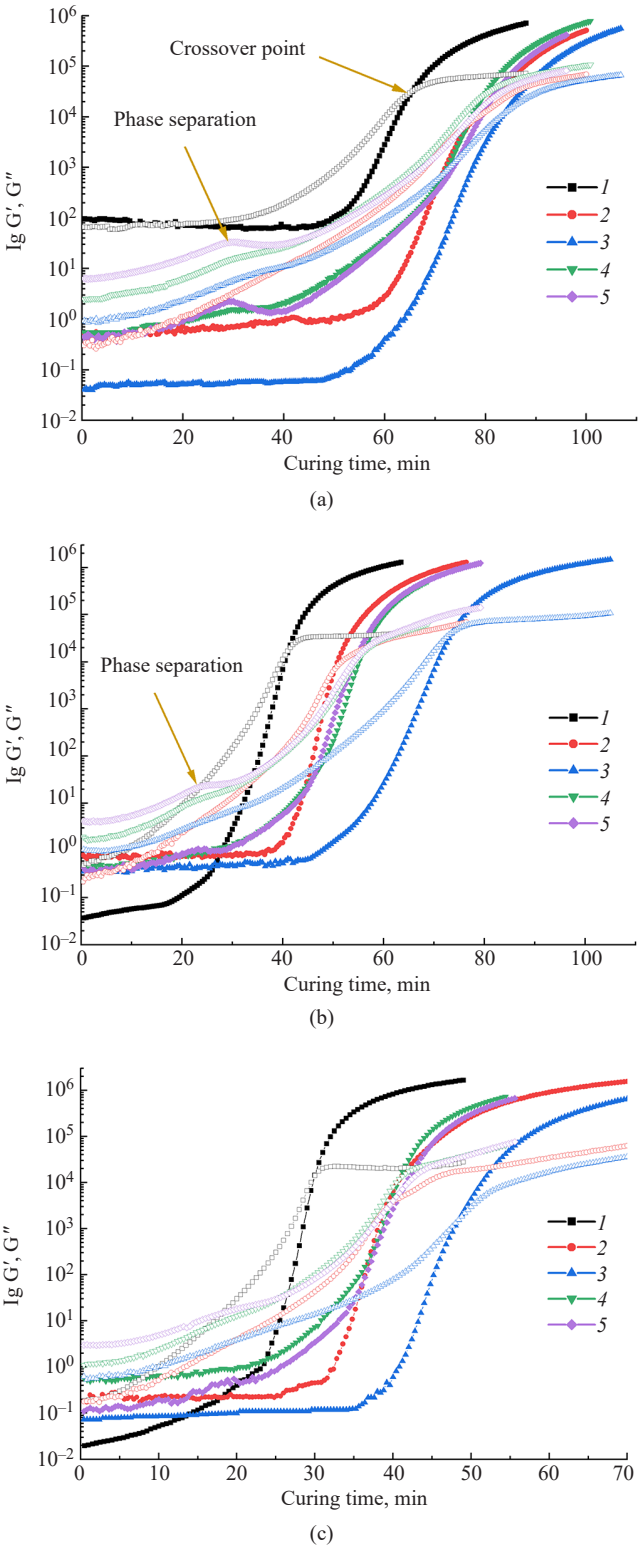


Fig. 1. Dependence of storage modulus G′ (solid symbols) and loss modulus G″ (hollow symbols) on curing time:
(*1*) ED-20,
(*2*) ED-20+PEI (5 pts. wt),
(*3*) ED-20+PEI (10 pts. wt),
(*4*) ED-20+PEI (15 pts. wt),
(*5*) ED-20+PEI (20 pts. wt),
at 160 (a),
170 (b), and
180°C (c)

data [15]. The table below summarizes the crossover point reach times calculated from Fig. 1.

Table. Times of reaching the crossover points of the studied binders

Sample	Time of the crossover point, min		
	160°C	170°C	180°C
ED-20	66	41	30
ED-20+PEI (5 pts. wt)	77	50	39
ED-20+PEI (10 pts. wt)	84	74	48
ED-20+PEI (15 pts. wt)	80	56	41
ED-20+PEI (20 pts. wt)	81	55	41

From Figs. 1a and 1b, it can be seen that in the system containing 20 pts. wt of PEI (curve *5*) at 160°C at the 29th min (Fig. 1a) and at 170°C at the 23rd min of the experiment (Fig. 1b), there is a decrease in the loss modulus value, which is related to the dynamic viscosity by the following relationship:

$$\eta' = \frac{G''}{\omega},$$

where η′ is dynamic viscosity, Pa·s; G″ is loss modulus, Pa; ω is frequency, rad/s.

This means that the dependence of the loss modulus has qualitatively the same character as the dependence of the dynamic viscosity under the condition of constant frequency during the experiment. Consequently, it can be assumed that the decrease in the loss modulus value is due to the release of the viscous component, PEI, from the reaction system into a separate phase. At this point, the curing process ceases to be homogeneous and begins to be heterogeneous. Then, due to the ongoing curing process, the loss modulus of the system increases again.

In the technology of reinforced plastics, the concept of binder pot-life parameter is taken as the time to reach a certain viscosity level, above which the binder is no longer able to impregnate the reinforcing filler. This parameter is often taken as ≈100 Pa·s [1, 11]. From Fig. 2, it can be concluded that a system containing 10 pts. wt of PEI (curve *3*) has an increased (about 15–27 min) pot-life compared to other binders studied in this work. As the "process window" for processing the material into composite products increases, this represents a clear advantage of the thermoplastic-modified binder in comparison withneat ED-20. Since epoxy binders are Newtonian fluids at elevated temperatures [15, 16], the complex viscosity can be fairly taken as the effective viscosity based on the Cox–Merz rule.

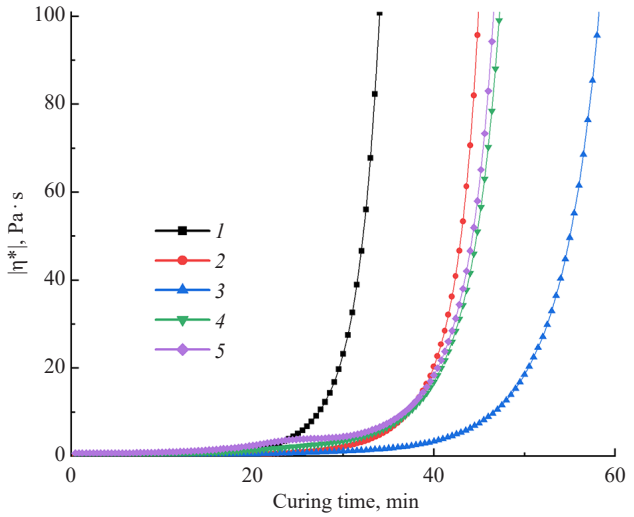


Fig. 2. Dependence of complex viscosity (|η*|) on curing time at 170°C:
(*1*) ED-20,
(*2*) ED-20+PEI (5 pts. wt),
(*3*) ED-20+PEI (10 pts. wt),
(*4*) ED-20+PEI (15 pts. wt),
(*5*) ED-20+PEI (20 pts. wt)

Since higher temperatures lead to more intensive curing processes, it would be expected that the limiting value of the storage modulus would be higher at 180°C. In practice, however, the limiting value of elastic modulus is found to be higher at 170°C, as shown in Fig. 3.

The point to bear in mind here is that the modulus of elasticity is affected by the temperature of the experiment. Since the modulus of elasticity is known to decrease with increasing temperature, so at 180°C, the decrease in the ultimate value of the modulus of elasticity due to the higher temperature prevails over its increase due to curing.

CONCLUSIONS

It has been shown that the addition of a thermoplastic modifier to an epoxy binder increases the gelation time, which is due both to the slowing down of the curing process in the presence of the thermoplastic, which dilutes the reaction system, as well as to the increased viscosity of the modified binder itself compared to the unmodified binder. The highest pot-life was recorded for the system modified with 10 pts. wt of PEI. The higher ultimate value of elastic modulus at a curing temperature of 170°C than that at 180°C is due to the dual effect of temperature.

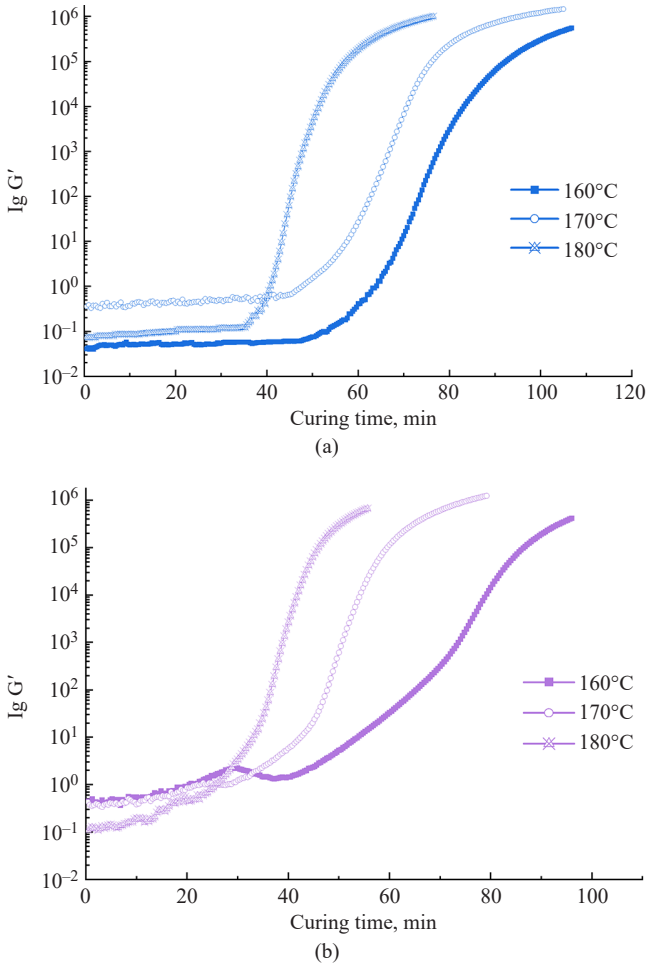


Fig. 3. Dependence of storage modulus (G′) on curing time at three temperatures: (a) ED-20+PEI (10 pts. wt), (b) ED-20+PEI (20 pts. wt)

Authors' contributions

S.V. Polunin—conducting experiments, processing the data obtained, discussing the results obtained, and participating in editing the text of the article.

K.A. Atamas—processing the obtained data, literature review on the topic of the article, writing and formatting the text of the article.

I.Yu. Gorbunova—research idea, planning experiments, analyzing and discussing the results, and editing the text of the article.

P.A. Morozova—conducting experiments and discussing the results obtained.

K.M. Marakhovsky—planning experiments, discussing the results obtained, and participating in editing the text of the article.

The authors declare no conflicts of interest.

REFERENCES

1. Kerber M.L., Vinogradov V.M., Golovkin G.S., *et al. Polimernye kompozitsionnye materialy: struktura, svoistva, tekhnologiya* (*Polymer Composite Materials: Structure, Properties, Technology*). St. Petersburg: Professiya; 2024. 712 p. (in Russ.). ISBN 978-5-91844-136-5
2. Chen F., Zhang Y., Sun T., Han C.C. Miscibility, Phase Separation and Mechanism of Phase Separatrion in Epoxy/Thermoplastic Blends. In: Parameswaranpillai J., Hameed N., Pionteck J., Woo E. (Eds.). *Handbook of Epoxy Blends*. Springer; 2017. P. 487–521. http://doi.org/10.1007/978-3-319-40043-3_17
3. Chen Z., Luo Z., Huang Z., Cai C., Tusiime R., Li Z., Wang H., Cheng C., Liu Y., Sun Z., Zhang H., Yu J. Synergistic toughen epoxy resin by incorporation of polyetherimide and amino groups grafted MWCNTs. *Composit. Commun*. 2020;21(8):100377. https://doi.org/10.1016/j.coco.2020.100377
4. Sun Z., Xu L., Chen Z., Wang Y., Tusiime R., Cheng C., Zhou S., Liu Y., Yu M., Zhang H. Enhancing the Mechanical and Thermal Properties of Epoxy Resin via Blending with Thermoplastic Polysulfone. *Polymers*. 2019;11(3):461–478. https://doi.org/10.3390/polym11030461
5. Yu G., Wu P. Effect of chemical modified graphene oxide on the phase separation behaviour and properties of an epoxy/polyetherimide binary system. *Polym. Chem*. 2014;5(1):96–104. https://doi.org/10.1039/C3PY00878A
6. Bresskaya A.D., Trofimov D.A., Simonov-Emel'yanov I.D., Shalgunov S.I., Sokolov V.I. Investigation of surface tension and contact angles for effective polymer binders based on epoxy oligomers and active diluents. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2020;15(3):47–57. https://doi.org/10.32362/2410-6593-2020-15-3-47-57
7. Muthalif M., Choe Y. Influence of Maleinized Polybutadiene on Adhesive Strenght and Toughness of Epoxy Resins. *Int. J. Polym. Sci*. 2022;2022(1):1–8. https://doi.org/10.1155/2022/9517467
8. Deng H., Yuan L., Gu A., Liang G. Facile strategy and mechanism of great toughening epoxy resin using polyethersulfone through controlling phase separation with microwave-assisted thermal curing technique. *J. Appl. Polym. Sci*. 2019;137(8):48394. http://doi.org/10.1002/app.48394
9. Shapagin A.V., Budylin N.Yu., Chalykh A.E., Solodilov V.I., Korokhin R.A., Poteryaev A.A. Phase Equilibrium, Morphology, and Physico-Mechanics in Epoxy-Thermoplastic Mixtures with Upper and Lower Critical Solution Temperatures. *Polymers*. 2021;13(1):35–47. https://doi.org/10.3390/polym13010035
10. Johnson L.M., Huffman N.D. Rheology of Epoxy/Thermoplastic Blends. In: Parameswaranpillai J., Hameed N., Pionteck J., Woo E. (Eds.). *Handbook of Epoxy Blends*. Springer; 2017. P. 613–648. http://doi.org/10.1007/978-3-319-40043-3_21
11. Arinina M.P., Kostenko V.A., Gorbunova I.Yu., *et al.* Kinetics of curing of epoxy oligomer by diaminodiphenyl Sulfone: Rheology and calorimetry. *Polym. Sci. Ser. A.* 2018;60(5):683–690. https://doi.org/10.1134/S0965545X18050012 [Original Russian Text: Arinina M.P., Kostenko V.A., Gorbunova I.Yu., Il'in S.O., Malkin A.Ya. Kinetics of curing of epoxy oligomer by diaminodiphenylsulfone. Rheology and calorimetry. *Vysokomolekulyarnye Soedineniya. Seriya A.* 2018;60(5):418–425 (in Russ.). https://doi.org/10.1134/S2308112018050012]
12. Cicala G., Mamo A., Latteri A., Recca G. Epoxy/thermoplastic blends: the effect of two different aromatic modifiers. *J. Mater. Des. Appl.* 2011;225(4):316–326. http://doi.org/10.1177/1464420711411397

СПИСОК ЛИТЕРАТУРЫ

1. Кербер М.Л., Виноградов В.М., Головкин Г.С., Горбаткина Ю.А., Крыжановский В.К., Куперман А.М., Симонов-Емельянов И.Д., Халиулин В.И., Бунаков В.А. *Полимерные композиционные материалы: структура, свойства, технология*. 6-е изд. СПб.: ЦОП «Профессия»; 2024. 712 с. ISBN 978-5-91844-136-5
2. Chen F., Zhang Y., Sun T., Han C.C. Miscibility, Phase Separation and Mechanism of Phase Separatrion in Epoxy/Thermoplastic Blends. In: Parameswaranpillai J., Hameed N., Pionteck J., Woo E. (Eds.). *Handbook of Epoxy Blends*. Springer; 2017. P. 487–521. http://doi.org/10.1007/978-3-319-40043-3_17
3. Chen Z., Luo Z., Huang Z., Cai C., Tusiime R., Li Z., Wang H., Cheng C., Liu Y., Sun Z., Zhang H., Yu J. Synergistic toughen epoxy resin by incorporation of polyetherimide and amino groups grafted MWCNTs. *Composit. Commun*. 2020;21(8):100377. https://doi.org/10.1016/j.coco.2020.100377
4. Sun Z., Xu L., Chen Z., Wang Y., Tusiime R., Cheng C., Zhou S., Liu Y., Yu M., Zhang H. Enhancing the Mechanical and Thermal Properties of Epoxy Resin via Blending with Thermoplastic Polysulfone. *Polymers*. 2019;11(3):461–478. https://doi.org/10.3390/polym11030461
5. Yu G., Wu P. Effect of chemical modified graphene oxide on the phase separation behaviour and properties of an epoxy/polyetherimide binary system. *Polym. Chem*. 2014;5(1):96–104. https://doi.org/10.1039/C3PY00878A
6. Бресская А.Д., Трофимов Д.А., Симонов-Емельянов И.Д., Шалгунов С.И., Соколов В.И. Исследование поверхностного натяжения и углов смачивания для создания эффективных полимерных связующих на основе эпоксидных олигомеров с активными разбавителями. *Тонкие химические технологии*. 2020;15(3):47–57. https://doi.org/10.32362/2410-6593-2020-15-3-47-57
7. Muthalif M., Choe Y. Influence of Maleinized Polybutadiene on Adhesive Strenght and Toughness of Epoxy Resins. *Int. J. Polym. Sci*. 2022;2022(1):1–8. https://doi.org/10.1155/2022/9517467
8. Deng H., Yuan L., Gu A., Liang G. Facile strategy and mechanism of great toughening epoxy resin using polyethersulfone through controlling phase separation with microwave-assisted thermal curing technique. *J. Appl. Polym. Sci*. 2019;137(8):48394. http://doi.org/10.1002/app.48394
9. Shapagin A.V., Budylin N.Yu., Chalykh A.E., Solodilov V.I., Korokhin R.A., Poteryaev A.A. Phase Equilibrium, Morphology, and Physico-Mechanics in Epoxy-Thermoplastic Mixtures with Upper and Lower Critical Solution Temperatures. *Polymers*. 2021;13(1):35–47. https://doi.org/10.3390/polym13010035
10. Johnson L.M., Huffman N.D. Rheology of Epoxy/Thermoplastic Blends. In: Parameswaranpillai J., Hameed N., Pionteck J., Woo E. (Eds.). *Handbook of Epoxy Blends*. Springer; 2017. P. 613–648. http://doi.org/10.1007/978-3-319-40043-3_21
11. Аринина М.П., Костенко В.А., Горбунова И.Ю., Ильин С.О., Малкин А.Я. Кинетика отверждения эпоксидного олигомера диаминодифенилсульфоном. Реология и калориметрия. *Высокомолекулярные соединения. Серия А.* 2018;60(5):418–425. https://doi.org/10.1134/S2308112018050012
12. Cicala G., Mamo A., Latteri A., Recca G. Epoxy/thermoplastic blends: the effect of two different aromatic modifiers. *J. Mater. Des. Appl.* 2011;225(4):316–326. http://doi.org/10.1177/1464420711411397
13. Polunin S.V., Gorbunova I.Yu., Kerber M.L., Khokhlova E.V., Kryuchkov I.A., Kravchenko T.P., Studying the Rheokinetics of Curing Processes in Epoxy Amine Binders Modified with Carding Polysulfon. *Polym. Sci. Ser. D*. 2023;16(4):824–829. http://doi.org/10.1134/S1995421223040275

13. Polunin S.V., Gorbunova I.Yu., Kerber M.L., Khokhlova E.V., Kryuchkov I.A., Kravchenko T.P., Studying the Rheokinetics of Curing Processes in Epoxy Amine Binders Modified with Carding Polysulfon. *Polym. Sci. Ser. D*. 2023;16(4):824–829. http://doi.org/10.1134/S1995421223040275
14. Lee S.-Y., Kang M.-J., Kim S.-H., Rhee K.-Y., Lee J.-H., Park S.-J. Roles of Small Polyetherimide Moieties on Thermal Stability and Fracture Toughness of Epoxy Blends. *Polymers*. 2021;13(19):3310–3320. http://doi.org/10.3390/polym13193310
15. Arinina M.P., Ilyin S.O., Makarova V.V., *et al.* Miscibility and rheological properties of epoxy resin blends with aromatic polyethers. *Polym. Sci. Ser. A*. 2015;57(2):177–185. https://doi.org/10.1134/S0965545X15020017
[Original Russian Text: Arinina M.P., Ilyin S.O., Makarova V.V., Kulichikhin V.G., Gorbunova I.Y., Kerber M.L. Miscibility and rheological properties of epoxy resin blends with aromatic polyethers. *Vysokomolekulyarnye Soedineniya. Seriya A*. 2015;57(2):152–161 (in Russ.). https://doi.org/10.1134/S2308112018050012]
16. Guo Q., Zhu P., Li G., Huang L., Zhang Yu., Lu D., Sun R., Wong C.P. One-pot synthesis of bimodal silica nanospheres and their effects on the rheological and thermal-mechanical properties of silica-epoxy composites. *RSC Adv*. 2015;5(62):50073–50081. https://doi.org/10.1039/C5RA06914A

14. Lee S.-Y., Kang M.-J., Kim S.-H., Rhee K.-Y., Lee J.-H., Park S.-J. Roles of Small Polyetherimide Moieties on Thermal Stability and Fracture Toughness of Epoxy Blends. *Polymers*. 2021;13(19):3310–3320. http://doi.org/10.3390/polym13193310
15. Аринина М.П., Ильин С.О., Макарова В.В., Горбунова И.Ю., Кербер М.Л., Куличихин В.Г. Совместимость и реологические свойства смесей эпоксидианового олигомера с ароматическими полиэфирами. *Высокомолекулярные соединения. Серия А*. 2015;57(2):152–161. https://doi.org/10.7868/S2308112015020017
16. Guo Q., Zhu P., Li G., Huang L., Zhang Yu., Lu D., Sun R., Wong C.P. One-pot synthesis of bimodal silica nanospheres and their effects on the rheological and thermal-mechanical properties of silica-epoxy composites. *RSC Adv*. 2015;5(62):50073–50081. https://doi.org/10.1039/C5RA06914A

About the authors

Stepan V. Polunin, Cand. Sci. (Chem.), Associate Professor, Department of Plastic Processing Technology, D.I. Mendeleev Russian University of Chemical Technology (RSTU) (9, Miusskaya pl., Moscow, 125047, Russia). E-mail: mcnion@gmail.com. Scopus Author ID 57214461159, ResearcherID AGU-0493-2022, RSCI SPIN-code 8265-8155, https://orcid.org/0000-0003-1732-9999

Kirill A. Atamas, Master Student, D.I. Mendeleev Russian University of Chemical Technology (RSTU) (9, Miusskaya pl., Moscow, 125047, Russia). E-mail: atamas.kirillandreich@yandex.ru. RSCI SPIN-code 9284-8979, https://orcid.org/0009-0002-6266-1624

Irina Yu. Gorbunova, Dr. Sci. (Chem.), Professor, Head of the Department of Plastic Processing Technology, D.I. Mendeleev Russian University of Chemical Technology (RSTU) (9, Miusskaya pl., Moscow, 125047, Russia). E-mail: giy161@yandex.ru. Scopus Author ID 7006042682, ResearcherID D-4732-2014, RSCI SPIN-code 6969-3346, https://orcid.org/0000-0002-0390-9100

Polina A. Morozova, Master Student, D.I. Mendeleev Russian University of Chemical Technology (RSTU) (9, Miusskaya pl., Moscow, 125047, Russia). E-mail: polinaalex1999@gmail.com. Scopus Author ID 58560493900, RSCI SPIN-code 9859-2958, https://orcid.org/0009-0003-0204-5667

Konstantin M. Marakhovsky, Cand. Sci. (Eng.), Head of the Laboratory for Testing Polymer Raw Materials and Plastic Products, Intersectoral Institute of Plastics Processing – NPO "Plastic" (20–10, Berezhkovskaya nab., Moscow, 121059, Russia). E-mail: kmara@npoplastic.ru. Scopus Author ID 57210255996, RSCI SPIN-code 8367-0770, https://orcid.org/0009-0004-2210-7076

Об авторах

Полунин Степан Владимирович, к.х.н., доцент кафедры технологии переработки пластмасс, ФГБОУ ВО «Российский химико-технологический университет им. Д.И. Менделеева» (125047, Россия, Москва, Миусская пл., д. 9). E-mail: mcnion@gmail.com. Scopus Author ID 57214461159, ResearcherID AGU-0493-2022, SPIN-код РИНЦ 8265-8155, https://orcid.org/0000-0003-1732-9999

Атамас Кирилл Андреевич, магистрант, ФГБОУ ВО «Российский химико-технологический университет им. Д.И. Менделеева» (125047, Россия, Москва, Миусская пл., д. 9). E-mail: atamas.kirillandreich@yandex.ru. SPIN-код РИНЦ 9284-8979, https://orcid.org/0009-0002-6266-1624

Горбунова Ирина Юрьевна, д.х.н., профессор, заведующий кафедрой технологии переработки пластмасс, ФГБОУ ВО «Российский химико-технологический университет им. Д.И. Менделеева» (125047, Россия, Москва, Миусская пл., д. 9). E-mail: giy161@yandex.ru. Scopus Author ID 7006042682, ResearcherID D-4732-2014, SPIN-код РИНЦ 6969-3346, https://orcid.org/0000-0002-0390-9100

Морозова Полина Алексеевна, магистрант, ФГБОУ ВО «Российский химико-технологический университет им. Д.И. Менделеева» (125047, Россия, Москва, Миусская пл., д. 9). E-mail: polinaalex1999@gmail.com. Scopus Author ID 58560493900, SPIN-код РИНЦ 9859-2958, https://orcid.org/0009-0003-0204-5667

Мараховский Константин Маркович, к.т.н., заведующий лабораторией испытаний полимерного сырья и изделий из пластмасс, АО «Межотраслевой институт переработки пластмасс – НПО «Пластик» (121059, Россия, Москва, Бережковская набережная, д. 20, стр. 10). E-mail: kmara@npoplastic.ru. Scopus Author ID 57210255996, SPIN-код РИНЦ 8367-0770, https://orcid.org/0009-0004-2210-7076

Translated from Russian into English by N. Isaeva
Edited for English language and spelling by Thomas A. Beavitt

Tonkie Khimicheskie Tekhnologii = Fine Chemical Technologies.
2024;19(6):536–546
ISSN 2686-7575 (Online)

Synthesis and processing of polymers and polymeric composites
Синтез и переработка полимеров и композитов на их основе

UDC 678.072:691.175.664:678.7
https://doi.org/10.32362/2410-6593-2024-19-6-536-546
EDN WISPPK

CC BY

RESEARCH ARTICLE

Study of the influence of ultra-high molecular weight polyethylene and high-density polyethylene on the properties and structure of ethylene propylene diene monomer rubber

Marina D. Sokolova✉, **Anna R. Khaldeeva, Maria L. Davydova, Aitalina F. Fedorova, Nikolay V. Shadrinov**

Federal Research Center "The Yakut Scientific Center of the Siberian Branch of the Russian Academy of Sciences," Institute of Oil and Gas Problems SB RAS, Yakutsk, 677007 Russia

✉ *Corresponding author, e-mail: marsokol@mail.ru*

Abstract

Objectives. The study set out to examine the impact of pre-mixed ultra-high molecular weight polyethylene (UHMWPE) and high-density polyethylene (HDPE) on a range of properties and structural characteristics of SKEPT-50 ethylene propylene diene monomer (EPDM) rubber.

Methods. The production of rubber mixtures involved the pre-mixing of rubber with UHMWPE and HDPE in a Brabender PL 2200-3 plasti-corder chamber (Germany) at a temperature of 160°C, for a period of 6 min, and with a rotor speed of 60 rpm. The polyethylene constituents were incorporated into the rubber compound at concentrations of 5, 10, and 15 pts. wt. The subsequent introduction of the principal constituents of the rubber mixture was conducted in an SYM laboratory mill (China) for a period of 30 min at a temperature of no more than 100°C. The vulcanization of the samples was conducted in an Y1000D vacuum hydraulic press (China) at a temperature of 185°C for a period of 35 min. The investigation of vulcanization and physical and mechanical properties was conducted in accordance with the established protocols. The analysis of the rubber supramolecular structure was conducted using a JEOL JSM-6840 LV scanning electron microscope (Japan).

Results. The results demonstrate that an increase in the proportion of HDPE and UHMWPE to 15 pts. wt leads to a notable enhancement in the hardness of the rubbers by 10 and 5 Shore A units, respectively. The frost resistance coefficient at −45°C demonstrates an increase with the incorporation of 10 pts. wt of HDPE to reach a value of 0.229, and a further increase with the incorporation of 15 pts. wt of UHMWPE to reach a value of 0.260. The degree of swelling of rubbers in a DOT-4 brake fluid environment is observed to decrease to 13% for rubbers with HDPE and 19% with UHMWPE. The degree of swelling of rubbers in the DOT-4 brake fluid environment is observed to decrease to 13% for rubbers with HDPE and 19% with UHMWPE. While an increase in the HDPE content results in a 5% increase in volumetric wear, an increase in the UHMWPE content is associated with a 45% decrease in volumetric wear. The introduction of UHMWPE was observed to result in the formation of inclusions of varying shapes and sizes within a range of 50–100 μm. The transition zone between UHMWPE and rubber is characterized by a smooth surface. No evidence of cracks or micro-tears between the polymer phases, which could potentially form during low-temperature splitting, was observed. This finding indicates the presence of favorable interfacial interactions, which can be linked to the observed enhancements in resistance to aggressive liquids and abrasion, as well as the improved tensile frost resistance coefficient. The supramolecular structure of rubber samples combined with HDPE is more pronounced and exhibits greater relief than that of the original rubber. This is indicative of a more uniform distribution within the matrix volume, which can be attributed to the high fluidity of the HDPE melt.

Conclusions. Rubbers modified with UHMWPE, in comparison with HDPE, exhibit enhanced resistance to wear, oil, and frost, while maintaining their elastic and strength properties. It was established that rubber containing 15 pts. wt of UHMWPE exhibits optimal properties and can thus be recommended for use in sealing rubber products.

© M.D. Sokolova, A.R. Khaldeeva, M.L. Davydova, A.F. Fedorova, N.V. Shadrinov, 2024

Keywords
ethylene propylene diene monomer rubber, rubber, high-density polyethylene, ultra-high molecular weight polyethylene, modification, physical and mechanical properties

Submitted: 26.07.2024
Revised: 09.09.2024
Accepted: 18.10.2024

For citation
Sokolova M.D., Khaldeeva A.R., Davydova M.L., Fedorova A.F., Shadrinov N.V. Study of the influence of ultra-high molecular weight polyethylene and high-density polyethylene on the properties and structure of ethylene propylene diene monomer rubber. *Tonk. Khim. Tekhnol.* = *Fine Chem. Technol*. 2024;19(6):536–546. https://doi.org/10.32362/2410-6593-2024-19-6-536-546

НАУЧНАЯ СТАТЬЯ

Исследование влияния сверхвысокомолекулярного полиэтилена и полиэтилена низкого давления на свойства и структуру резин на основе этиленпропилендиенового каучука

М.Д. Соколова✉, А.Р. Халдеева, М.Л. Давыдова, А.Ф. Федорова, Н.В. Шадринов

Федеральный исследовательский центр «Якутский научный центр Сибирского отделения Российской академии наук», Институт проблем нефти и газа СО РАН, Якутск, 677007 Россия

✉ *Автор для переписки, e-mail: marsokol@mail.ru*

Аннотация

Цели. Изучение влияния сверхвысокомолекулярного полиэтилена (СВМПЭ) и полиэтилена низкого давления (ПЭНД) на комплекс свойств и структуру резин на основе этиленпропилендиенового каучука марки СКЭПТ-50.

Методы. Резиновые смеси изготавливали путем предварительного смешения каучука с СВМПЭ и ПЭНД в камере пластикордера BRABENDER PL 2200-3 (Германия) при температуре 160°C в течение 6 мин и скорости вращения роторов 60 об/мин. Полиэтилены вводили в количестве 5, 10 и 15 мас. ч. на 100 мас. ч. каучука. Последующее введение основных ингредиентов резиновой смеси производилось на лабораторных вальцах SYM (Китай) в течение 30 мин при температуре не более 100°C. Вулканизацию образцов проводили в вакуумном гидравлическом прессе Y1000D (Китай) при температуре 185°C в течение 35 мин. Исследование вулканизационных и физико-механических свойств проведено стандартными методами. Исследование надмолекулярной структуры резин проведено с помощью сканирующего электронного микроскопа JEOL JSM-6840 LV (Япония).

Результаты. Показано, что с увеличением содержания ПЭНД и СВМПЭ до 15 мас. ч. твердость резин повышается на 10 и 5 единиц по Шору А соответственно. Коэффициент морозостойкости при −45°C увеличивается, достигая значений 0.229 при введении 10 мас. ч. ПЭНД и 0.260 при введении 15 мас. ч. СВМПЭ. Степень набухания резин в среде тормозной жидкости DOT-4 снижается до 13% у резин с ПЭНД и 19% со СВМПЭ. Исследование стойкости образцов резин к абразивному износу выявило различия в износостойкости в зависимости от вида термопласта: с увеличением содержания ПЭНД объемный износ повышается на 5% и снижается на 45% при увеличении содержания СВМПЭ. Исследования надмолекулярной структуры показали, что при введении СВМПЭ появляются включения разнообразной формы с размерами в пределах 50–100 мкм. Переходная зона между СВМПЭ и каучуком достаточно плавная, трещин и микроразрывов между фазами полимеров, которые могли бы образоваться в процессе низкотемпературного раскалывания, не наблюдается. Это свидетельствует об удовлетворительном межфазном взаимодействии и объясняет повышение стойкости к агрессивной жидкости и абразивному истиранию, а также увеличение коэффициента морозостойкости при растяжении. Образцы резин с ПЭНД по сравнению с исходной резиной имеют более выраженную и рельефную надмолекулярную структуру без видимых включений, что свидетельствует о более равномерном распределении в объеме матрицы за счет высокой текучести расплава ПЭНД.

Выводы. Резины, модифицированные СВМПЭ, по сравнению с ПЭНД обладают более высокими показателями износо-, масло- и морозостойкости при сохранении упруго-прочностных показателей. Установлено, что резина, содержащая 15 мас. ч. СВМПЭ, обладает наилучшим комплексом свойств и может быть рекомендована для использования в производстве уплотнительных резинотехнических изделий.

Ключевые слова
этиленпропилендиеновый каучук, резина, полиэтилен низкого давления, сверхвысокомолекулярный полиэтилен, модификация, физико-механические свойства

Поступила: 26.07.2024
Доработана: 09.09.2024
Принята в печать: 18.10.2024

Для цитирования

Соколова М.Д., Халдеева А.Р., Давыдова М.Л., Федорова А.Ф., Шадринов Н.В. Исследование влияния сверхвысокомолекулярного полиэтилена и полиэтилена низкого давления на свойства и структуру резин на основе этиленпропилендиенового каучука. *Тонкие химические технологии*. 2024;19(6):536–546. https://doi.org/10.32362/2410-6593-2024-19-6-536-546

INTRODUCTION

The principal focus of contemporary elastomer chemistry and technology concerns the modification of rubbers with additives to create elastomeric materials having enhanced characteristics to support a broader range of applications. One of the most effective methods for modifying the properties of rubbers is to combine them with thermoplastic polymers, including polyethylene, polypropylene, and polyvinyl chloride. The potential of thermoplastic polymers as modifying additives in rubber and rubber-based materials has been demonstrated in numerous studies by various authors [1–4]. Nevertheless, the problem continues to be of both scientific and practical interest due to the advancement of technologies for the production of novel thermoplastic and rubber materials and the potential for obtaining materials with defined properties.

As has been demonstrated in previous studies [1, 3], the enhancement of specific material properties during modification is contingent upon a high level of interaction at the elastomer–filler phase interface. This is particularly evident when a developed transition layer is formed at this interface, which depends on the compatibility of the polymers involved. Nevertheless, it remains a challenging endeavor to identify a compatible combination of high-molecular-weight rubber and polymer components for optimal distribution and interaction at the phase interface.

Due to their chemical resistance, high strength, operational viability across a wide temperature range, resilience to ozone, heat, atmospheric conditions, and frost, as well as market availability and relatively low cost [5–8], ethylene propylene diene monomer (EPDM) rubbers are of particular interest in the development of frost-resistant rubbers that can function effectively in the presence of aggressive environments. EPDM is an amorphous and nonpolar rubber that exhibits a specific affinity with thermoplastic polyolefins that possess analogous polarity and solubility parameters [7].

In this regard, the aim of the work is to study the effect of ultra-high molecular weight polyethylene (UHMWPE) and high-density polyethylene (HDPE) additions on the complex properties and structure of rubbers based on EPDM rubber of the SKEPT-50 brand. The selection is based on the fact that UHMWPE, which is distinguished by a considerable length of macromolecules with minimal branching, exhibits a lower degree of crystallinity, as well as offering high strength, wear resistance, frost resistance, resilience to shock loads, and a low friction coefficient [9–11]. Consequently, HDPE exhibits a high degree of density, hardness, and rigidity. It is important that the melting of HDPE and UHMWPE occurs in the same temperature range as the process of vulcanization of EPDM (130–150°C) [1].

MATERIALS AND METHODS

Triple ethylene propylene diene rubber of the SKEPT-50 brand produced by *Ufaorgsintez* (Russia) with mass fractions of propylene units 42–50% and dicyclopentadiene units 5.8–7.2% was used as the basis of rubber mixtures (TU 2294-087-05766563-2010). UHMWPE of the GUR 4113 brand with a medium-viscosity molecular weight of $3.9 \cdot 10^6$ g/mol produced by *Celanese* (Germany) and HDPE of the 273-83 brand with a medium-viscosity molecular weight of $0.5 \cdot 10^6$ g/mol produced by *Kazanorgsintez* (Russia) were selected as modifying additives. Polyethylene additions were introduced in amounts of 5, 10, and 15 pts. wt per 100 pts. wt of rubber. Formulations of rubber compounds based on SKEPT-50 are presented in Table 1. The following ingredients were also used to produce rubber mixtures: carbon black of the N550 brand produced by *Ivanovo Carbon Black and Rubber* (Russia) (CAS No. 1333-86-4), zinc oxide produced by *Chelyabinsk Chemical Plant "OXIDE"* (Russia) (CAS No. 1314-13-2), stearic acid produced by *Component-Reaktiv* (Russia) (CAS No. 57-11-4), altax produced by *Ningbo Actmix Rubber Chemicals Co.* (China) (CAS No. 120-78-5) and sulfur produced by *Kaspiygas* (Russia) (CAS No. 7704-34-9).

The rubber mixtures (2–7) are prepared by pre-mixing rubber with UHMWPE and HDPE in the Brabender PL 2200-3 plasti-corder chamber (*Brabender*, Germany) at a temperature of 160°C for 6 min and a rotor speed of 60 rpm. The subsequent introduction of the primary constituents of the rubber mixture was conducted on SYM laboratory rollers (*Yi Tzung*, China) for a period of 30 min at a temperature of no more than 100°C. The samples were then subjected to vulcanization in a vacuum hydraulic press Y1000D (*Tung Yu*, China) at a temperature of 185°C for a duration of 35 min. The optimal temperature and duration of vulcanization of rubber compounds were selected on the basis of the findings of studies into the vulcanization characteristics.

Table 1. Formulation of rubber compounds based on SKEPT-50

No.	Ingredients	Weight parts per 100 weight parts of rubber						
		1	2	3	4	5	6	7
1	SKEPT-50	100.0	100.0	100.0	100.0	100.0	100.0	100.0
2	HDPE 273-83	–	5.0	–	10.0	–	15.0	–
3	UHMWPE GUR 4113	–	–	5.0	–	10.0	–	15.0
4	Carbon black N550	50.0	50.0	50.0	50.0	50.0	50.0	50.0
5	Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0
6	Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5
7	Altax	1.5	1.5	1.5	1.5	1.5	1.5	1.5
8	Sulfur	2.0	2.0	2.0	2.0	2.0	2.0	2.0

The vulcanization characteristics of rubber compounds were determined on a rotor-free analyzer for the recyclability of rubbers RPA 2000 from *Alpha Technologies* (USA) at a temperature of 185°C, a frequency of 1.7 Hz and a deformation amplitude of 0.5° for 50 min in accordance with GOST R 54547-2011[1]. The determination of physical and mechanical parameters, as well as the study of tensile frost resistance were carried out on the UTS-20K test machine (*UTS Testsysteme*, Germany) in accordance with GOST 270-75[2] and GOST 408-78[3], respectively. The resistance to ageing of the materials under the influence of static compression deformation was determined in accordance with GOST 9.029-74[4] at 20% compression and a temperature of 100°C. The wear resistance of the rubbers was evaluated by the method of determining abrasion resistance in accordance with GOST 23509-79[5] on an AR-40 friction machine (*Compart*, Russia). Shore A hardness was determined according to GOST 263-75[6]. The degree of swelling of vulcanizates in a medium of DOT-4 brake fluid (*LUXE*, Russia) was determined according to GOST 9.030-74[7]. The supramolecular structure of rubbers was studied using a JEOL JSM-6840 LV scanning electron microscope (*JEOL*, Japan) on low-temperature chips of rubber samples.

RESULTS AND DISCUSSION

Vulcanization characteristics of rubber compounds based on SKEPT-50 are shown in Table 2.

The study of the vulcanization kinetics of rubber compounds has shown that a decrease in the maximum torque (S'_{max}) as compared to the initial compound can be achieved by introducing modifying additives. An increase in the content of HDPE to 15 pts. wt leads to a decrease in S'_{max} by 29%, while an increase

1 GOST R 54547-2011. National Standard of the Russian Federation. Rubber compounds. Measurement of vulcanization characteristics with the rotorless cure meters. Moscow: Standartinform; 2018.

2 GOST 270-75. Interstate Standard. Rubber. Method of the determination elastic and tensile stress-strain properties. Moscow: Standartinform; 2008.

3 GOST 408-78. State Standard of the USSR. Rubber. Methods for determination of low temperature resistance at extension. Moscow: Izdatelstvo standartov; 1985.

4 GOST 9.029-74. State Standard of the USSR. Unified system of corrosion and ageing protection. Vulcanized rubbers. Method of testing of resistance to ageing under static deformation of compression. Moscow: Izdatelstvo standartov; 1982.

5 GOST 23509-79. Interstate Standard. Rubber. Method for the determination of abrasion resistance under slipping a renewing surface. Moscow; IPK Izdatelstvo standartov; 2001.

6 GOST 263-75. State Standard of the USSR. Rubber. Method for the determination of Shore A hardness. Moscow: Izdatelstvo standartov; 1989.

7 GOST 9.030-74. Interstate Standard. Unified system of corrosion and ageing protection. Vulcanized rubbers. Method of testing of resistance to attack by corrosive media in limp state. Moscow: Standartinform; 2003.

Table 2. Vulcanization characteristics of rubber compounds

No.	Properties	Original rubber	5 pts. wt		10 pts. wt		15 pts. wt	
			HDPE	UHMWPE	HDPE	UHMWPE	HDPE	UHMWPE
		1	2	3	4	5	6	7
1	S'_{max}, dN·m	15.48	13.46	14.15	11.89	13.78	11.06	14.03
2	S'_{min}, dN·m	1.29	1.11	1.26	1.01	1.33	0.98	1.44
3	$S'_{max} - S'_{min}$, dN·m	14.19	12.35	12.89	10.88	12.43	10.08	12.59
4	T_5, min	2.13	2.24	2.24	2.28	2.23	2.28	2.22
5	T_{90}, min	18.78	17.74	17.49	18.13	17.80	18.58	18.38
6	R_V, min^{-1}	6.01	6.45	6.56	6.31	6.42	6.13	6.19

Note: S'_{max} is the maximum torque; S'_{min} is the minimum torque; $S'_{max} - S'_{min}$ is the torque difference; T_5 is the time of onset of scorching; T_{90} is the time to achieve optimum vulcanization; R_V is the vulcanization rate.

in the content of UHMWPE reduces it by 11%. The introduction of HDPE leads to a gradual decrease in the minimum torque (S'_{min}), which indicates a decrease in the viscosity of rubber mixtures [12–13] due to increased melt fluidity; conversely, the introduction of UHMWPE leads to an increase in the viscosity of rubber mixtures. This is due to the length of the polymer chains, which ensures transformation of UHMWPE into a highly elastic state rather than a viscous state upon heating [2, 14]. The difference between the maximum and minimum torque ($S'_{max} - S'_{min}$) characterizes the cross-linking density in rubber [15–16]. The maximum density of the cross-linking is recorded in the original rubber. The smallest difference is characterized by rubber compounds containing HDPE. This behavior of HDPE-filled rubbers can be explained in terms of the better distribution of HDPE in the elastomer matrix, which is achieved during the high-temperature mixing of rubber with HDPE powder due to the high fluidity of its melt to manifest a shielding effect of the rubber macromolecules from the sulfur vulcanizing system [2]. As the concentration of HDPE increases, this effect increases together with a decrease in the cross-link density. In turn, UHMWPE, which takes the form of micro-volumes in the volume of the matrix, additionally locally hinders the process of cross-linking of rubber macromolecules through sulfur bridges, which also leads to a slight decrease in $S'_{max} - S'_{min}$ as compared to the original rubber. In both cases, the introduction of the studied thermoplastics leads to an increase in the time of the mixtures in the viscous state (T_5) and the vulcanization rate (R_V), thus reducing the time for achieving optimum vulcanization (T_{90}).

Table 3 presents the physical and mechanical and low-temperature characteristics of vulcanizates based on SKEPT-50.

A study of the physical and mechanical properties of rubbers has shown that with the introduction of polyethylene and increase in its content, both the conditional stress at 100% elongation (f_{100}) and the Shore A hardness (H) of the vulcanizates increase. Compared to the original rubber, rubber materials with 15 pts. wt of HDPE and UHMWPE have f_{100} values that are 1.4 times higher and Shore A hardness that is 10 and 5 units higher, respectively. At the same time, the conditional tensile strength (f_{st}) and elongation at break (ε_e) values remain close to those of the original rubber.

Studies of the low-temperature properties of vulcanizates have shown that the maximum coefficient of frost resistance (K_{frost}) are at −45°C for rubbers containing UHMWPE: the higher the UHMWPE content, the higher the frost resistance value K_{frost}. This is due to the fact that, compared to HDPE, UHMWPE has a more developed amorphous region with interlacing of long macromolecules and through macromolecules (connecting crystallites), giving the material high elasticity and frost resistance. Therefore, it is likely that the amorphous phase of UHMWPE contributes to freeze resistance at low temperatures when the rubber macromolecules lose their flexibility [17]. Rubbers with HDPE (2, 6) have a frost resistance coefficient under tension of less than 0.20, which indicates insufficient frost resistance of the rubber at a given temperature.

It is known [18] that the resistance of rubber to aggressive media is primarily determined by the nature of

Table 3. Properties of vulcanizates based on SKEPT-50

No.	Properties	Original rubber	5 pts. wt		10 pts. wt		15 pts. wt	
			HDPE	UHMWPE	HDPE	UHMWPE	HDPE	UHMWPE
		1	2	3	4	5	6	7
1	f_{st}, MPa	18.1	17.5	18.9	17.7	16.8	19.6	18.6
2	f_{100}, MPa	2.8	3.2	3.0	3.3	3.3	3.8	3.8
3	ε_e, %	516	492	528	496	466	585	487
4	K_{frost} at −45°C	0.240	0.199	0.230	0.229	0.247	0.173	0.260
5	H, Shore A scale	62	65	63	67	66	72	67
6	RRCS (100°C × 24 h), %	52	51	37	54	53	51	51
7	ΔM in DOT-4 (100°C × 72 h), %	1.78	1.61	1.71	1.60	1.58	1.55	1.43

Note: f_{st} is the conditional tensile strength; f_{100} is the conditional stress at 100% elongation; ε_e is the relative elongation at break; K_{frost} is the coefficient of frost resistance during tension; H is the Shore A hardness; RRCS is the relative residual compressive strain at 20% compression; ΔM is the degree of swelling.

the rubber. At the same time, the components that make up rubber have a significant impact on the behavior of rubber materials in aggressive environments. Due to its chemical nature, EPDM has high resistance to the action of polar media and low resistance to aliphatic, aromatic, and nonpolar solvents [7, 19]. In order to assess the resistance of rubber to aggressive environments, we selected a polar glycol-based brake fluid DOT-4 Arctic Extreme manufactured by *LUXE* (Russia) for use in hydraulic brakes and clutches of cars with disc and drum braking systems. The results of the study showed that all rubbers of compositions 1–7 in the DOT-4 medium exhibited high resistance. Despite the low degree of cross-linking, the degree of swelling of the rubber decreases to 13% for HDPE and 19% for UHMWPE at increased concentrations of these additives. It is likely that the high molecular weights of the polymers contribute to a reduction in the degree of swelling.

An important characteristic that allows evaluating the relaxation properties and sealing ability of rubbers is the amount of relative residual compression strain (RRCS). For rubbers 2, 4–7, the RRCS values are at the level of the original rubber, while rubber 3, which contains 5 pts. wt UHMWPE, exhibits a decrease in RRCS up to 37%.

One of the approaches to reducing rubber wear and improving performance is to increase abrasion resistance. Figure 1 shows the results of the abrasion resistance measurements of the studied rubbers.

The study of the resistance of rubber samples to abrasive wear revealed differences in wear resistance

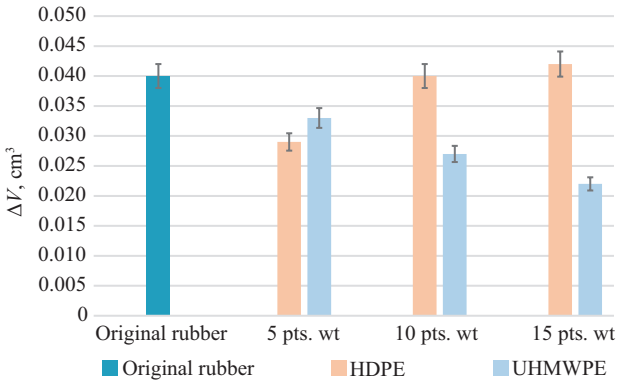


Fig. 1. Volumetric wear of rubber due to abrasive abrasion

depending on the type of polyethylene addition. When 5 pts. wt of both HDPE and UHMWPE were added to EPDM, volumetric wear was reduced by approximately 28% and 18%, respectively, as compared to the original rubber. The improved volumetric wear with increased HDPE content may additionally be due to a decrease in the cross-linking density of the rubber when HDPE is introduced. Increasing the UHMWPE content has a positive effect on the wear resistance of rubber. With the introduction of 15 pts. wt, volumetric wear is reduced by 45%. This is most likely due to the high tribotechnical properties of the UHMWPE itself.

Micrographs of low-temperature chips of rubbers containing modifying polyethylene additives obtained using a JEOL JSM-6840 LV scanning electron microscope are shown in Fig. 2.

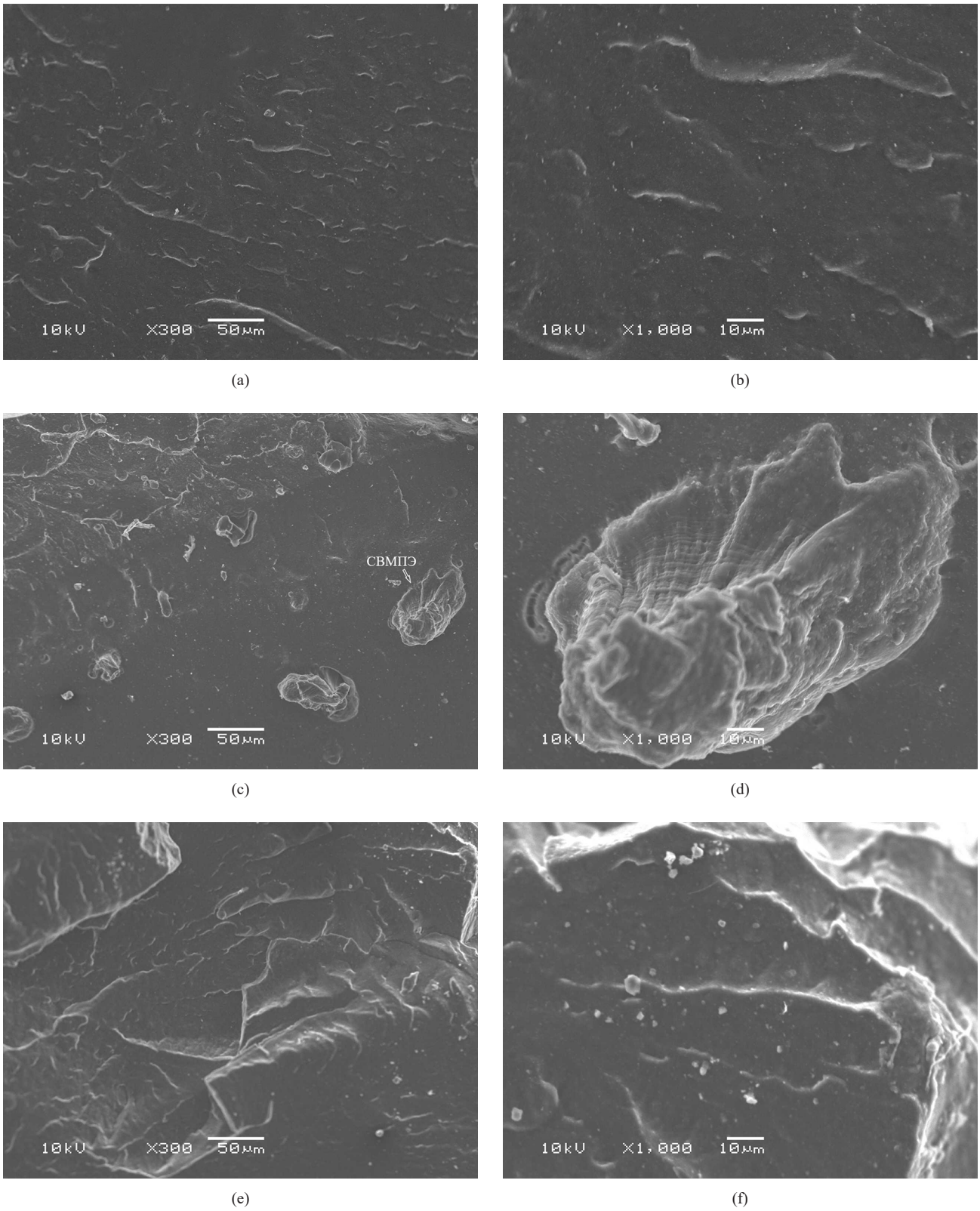


Fig. 2. Microphotographs of rubber based on SKEPT-50 (a, b);
SKEPT-50 + 15 pts. wt of UHMWPE (c, d);
SKEPT-50 + 15 pts. wt of HDPE (e, f)
at magnifications 300× (left) and 1000× (right)

Figure 2 shows that the original rubber initially has a homogeneous structure (Figs. 2a, 2b). Following the introduction of UHMWPE, inclusions of various shapes with sizes ranging from 50–100 μm appear (Figs. 2c, 2d). In samples containing UHMWPE, the transition zone between UHMWPE and rubber appears quite smooth without any cracks or microfractures between the phases of polymers that could form during low-temperature splitting. This indicates satisfactory interfacial interaction to explain the increased resistance to aggressive liquids and abrasive wear, as well as an increase in the coefficient of frost resistance under tension [2]. The samples of HDPE rubber (Figs. 2e, 2f) have a more pronounced and embossed supramolecular structure as compared to the original rubber. The absence of visible inclusions as manifested in the UHMWPE samples indicates a more uniform distribution in the volume of the matrix due to the high fluidity of the HDPE melt.

CONCLUSIONS

A comparative assessment of the effect of HDPE 273-83 and UHMWPE GUR 4113 additions on the complex of technical properties of rubbers based on SKEPT-50 was carried out. UHMWPE modified rubbers, in comparison with HDPE, have higher wear, oil and frost resistance while maintaining elastic strength characteristics due to satisfactory interfacial interaction between UHMWPE and rubber. The rubber compound containing 15 pts. wt of UHMWPE had the best set of properties and can be recommended for use in the manufacture of sealing rubber products. This demonstrates the potential of using UHMWPE and HDPE as modifying additives to improve the performance of EPDM-based rubbers.

Acknowledgments

The research was supported by the Head of the Republic of Sakha (Yakutia) (Agreement No. 02/1038) using the scientific equipment of the Center for Collective Use of the Federal Research Center “Yakut Scientific Center of the Siberian Branch of the Russian Academy of Sciences.”

Authors’ contributions

M.D. Sokolova—guidance and scientific consulting, editing the release version of the article.

A.R. Khaldeeva—conducting experimental studies, processing and analyzing the data obtained, writing the text of the article, and preparing materials for publication.

M.L. Davydova—processing and analysis of the obtained data, editing the article text.

A.F. Fedorova—processing and analysis of the data obtained, editing the text of the article.

N.V. Shadrinov—management at all stages of work, editing the article text.

The authors declare no conflicts of interest.

REFERENCES

1. Ammosova O.A., Argunova A.G., Botvin G.V. *et al. Modifitsirovannye polimernye i kompozitsionnye materialy dlya severnykh uslovii* (*Modified Polymer and Composite Materials for Northern Conditions*). Novosibirsk: Nauka; 2017. 217 p. (in Russ.). ISBN 978-5-7692-1527-8
2. Shadrinov N.V., Fedorova A.F., Gogolev V.D. Comparative analysis of effect of HDPE and UHMWPE on properties of nitrile butadiene rubber. *Khimicheskaya Tekhnologiya = Chemical Technology*. 2024;25(1):8–14 (in Russ.). https://doi.org/10.31044/1684-5811-2024-25-1-8-14
3. Shvarts A.G., Dinzburg B.N. *Sovmeshchenie kauchukov s plastikami i sinteticheskimi smolami* (*Combination of Rubbers with Plastics and Synthetic Resins*). Moscow: Khimiya; 1972. 224 p. (in Russ.).
4. Chernyshov S.V., Lyusova L.R., Makhmudova S.R., Zharylganova M.B., Konyaeva L.A. The effect of high-density polyethylene on the properties of elastomeric materials made of synthetic polyisoprene. *Kauchuk i Rezina*. 2023;82(5):242–247 (in Russ.). https://doi.org/10.47664/0022-9466-2023-82-5-242-247
5. Semenova S.N., Chaykun A.M., Suleymanov R.R. Ethylene-propylene-diene rubber and its use in rubber materials for special purposes. *Aviatsionnye materialy i tekhnologii = Aviation Materials and Technologies*. 2019;56(3):23–30 (in Russ.). http://doi.org/10.18577/2071-9140-2019-0-3-23-30
6. Lee S.-H., Park G.-W., Kim H.-J., Chung K., Jang K.-S. Effects of Filler Functionalization on Filler-Embedded Natural Rubber/Ethylene-Propylene-Diene Monomer Composites. *Polymers.* 2022;14(17):3502. https://doi.org/10.3390/polym14173502
7. Kablov E.N., Semenova S.N., Suleymanov R.R., Chaykun A.M. Prospects for the use of ethylene-propylene-diene rubber as part of cold resistant rubber. *Trudy VIAM = Proceedings of VIAM.* 2019;84(12):29–36 (in Russ.). https://doi.org/10.18577/2307-6046-2019-0-12-29-36
8. Eliseev O.A., Chaykun A.M., Buznik V.M., Sokolova M.D., Popov S.N. The basic principles of creation of formula cold-resistant rubbers stock for the products maintained in the conditions of the Arctic climate. *Perspektivnye Materialy.* 2015;11:5–18 (in Russ.).
9. Valueva M.I., Zhelezina G.F., Gulyaev I.N. Increased wear-resistance polymer composite materials based on ultra-high molecular weight polyethylene. *Vse materialy. Entsiklopedicheskii spravochnik = All Materials. Encyclopedic Reference Manual.* 2017;6:23–29 (in Russ.).
10. Samad M.A. Recent Advances in UHMWPE/UHMWPE Nanocomposite/UHMWPE Hybrid Nanocomposite Polymer Coatings for Tribological Applications: A Comprehensive Review. *Polymers.* 2021;13(4):608. https://doi.org/10.3390/polym13040608
11. Yue Q., Gao R., Song Z., Gou Q. Recent Advancements in the Synthesis of Ultra-High Molecular Weight Polyethylene via Late Transition Metal Catalysts. *Polymers.* 2024;16(12):1688. https://doi.org/10.3390/polym16121688
12. Yahaya L.E., Adebowale K.O., Olu-Owolabi B.I. Cure characteristics and rheological properties of modified kaolin-natural rubber composites. *Am. Chem. Sci. J.* 2014;4(4):472–480. http://doi.org/10.9734/ACSJ/2014/6575
13. Shadrinov N.V., Borisova A.A., Khaldeeva A.R., Antoev K.P. Influence of the technological mode of mixing and curing system on the properties of compositions based on nitrile rubber and ultra-high molecular weight polyethylene. *Perspektivnye Materialy*. 2023;2:77–86 (in Russ.). https://doi.org/10.30791/1028-978X-2023-2-77-86

СПИСОК ЛИТЕРАТУРЫ

1. Аммосова О.А., Аргунова А.Г., Ботвин Г.В. и др. *Модифицированные полимерные и композиционные материалы для северных условий*. Новосибирск: Наука; 2017. 217 с. ISBN 978-5-7692-1527-8
2. Шадринов Н.В., Федорова А.Ф., Гоголев В.Д. Сравнительный анализ влияния ПЭНД и СВМПЭ на свойства бутадиен-нитрильной резины. *Химическая технология*. 2024;25(1):8–14. https://doi.org/10.31044/1684-5811-2024-25-1-8-14
3. Шварц А.Г., Динзбург Б.Н. *Совмещение каучуков с пластиками и синтетическими смолами*. М.: Химия; 1972. 224 с.
4. Чернышев С.В., Люсова Л.Р., Махмудова С.Р., Жарылганова М.Б., Коняева Л.А. Влияние полиэтилена высокой плотности на свойства эластомерных материалов из синтетического полиизопрена. *Каучук и резина*. 2023;82(5):242–247. https://doi.org/10.47664/0022-9466-2023-82-5-242-247
5. Семенова С.Н., Чайкун А.М., Сулейманов Р.Р. Этилен-пропилендиеновый каучук и его применение в резинотехнических материалах специального назначения. *Авиационные материалы и технологии*. 2019;56(3):23–30. http://doi.org/10.18577/2071-9140-2019-0-3-23-30
6. Lee S.-H., Park G.-W., Kim H.-J., Chung K., Jang K.-S. Effects of Filler Functionalization on Filler-Embedded Natural Rubber/Ethylene-Propylene-Diene Monomer Composites. *Polymers.* 2022;14(17):3502. https://doi.org/10.3390/polym14173502
7. Каблов Е.Н., Семенова С.Н., Сулейманов Р.Р., Чайкун А.М. Перспективы применения эиленпропилендиенового каучука в составе морозостойкой резины. *Труды ВИАМ*. 2019;84(12):29–36. https://doi.org/10.18577/2307-6046-2019-0-12-29-36
8. Елисеев О.А., Чайкун А.М., Бузник В.М., Соколова М.Д., Попов С.Н. Основные принципы построения рецептур морозостойких резин для изделий, эксплуатируемых в условиях арктического климата. *Перспективные материалы*. 2015;11:5–18.
9. Валуева М.И., Железина Г.Ф., Гуляев И.Н. Полимерные композиционные материалы повышенной износостойкости на основе сверхвысокомолекулярного полиэтилена. *Все материалы. Энциклопедический справочник*. 2017;6:23–29.
10. Samad M.A. Recent Advances in UHMWPE/UHMWPE Nanocomposite/UHMWPE Hybrid Nanocomposite Polymer Coatings for Tribological Applications: A Comprehensive Review. *Polymers.* 2021;13(4):608. https://doi.org/10.3390/polym13040608
11. Yue Q., Gao R., Song Z., Gou Q. Recent Advancements in the Synthesis of Ultra-High Molecular Weight Polyethylene via Late Transition Metal Catalysts. *Polymers.* 2024;16(12):1688. https://doi.org/10.3390/polym16121688
12. Yahaya L.E., Adebowale K.O., Olu-Owolabi B.I. Cure characteristics and rheological properties of modified kaolin-natural rubber composites. *Am. Chem. Sci. J.* 2014;4(4):472–480. http://doi.org/10.9734/ACSJ/2014/6575
13. Шадринов Н.В., Борисова А.А., Халдеева А.Р., Антоев К.П. Влияние технологического режима смешения и вулканизующей системы на свойства композиций на основе бутадиен-нитрильного каучука и сверхвысокомолекулярного полиэтилена. *Перспективные материалы*. 2023;2:77–86. https://doi.org/10.30791/1028-978X-2023-2-77-86
14. Белокурова А.П., Агеева Т.А. *Химия и технология получения полиолефинов*. Иваново: Иван.гос. хим.-технол. ун-т.; 2011. 126 с. ISBN 978-5-9616-0399-4

14. Belokurova A.P., Ageeva T.A. *Khimiya i tekhnologiya polucheniya poliolefinov* (*Chemistry and Technology for Producing Polyolefins*). Ivanovo: Ivanovo State University of Chemistry and Technology; 2011. 126 p. (in Russ.). ISBN 978-5-9616-0399-4
15. Novakov I.A., Vol'fson S.I., Novopol'tseva O.M., Krakshin M.A. *Reologicheskie i vulkanizatsionnye svoistva elastomernykh kompozitsii* (*Rheological and Vulcanization Properties of Elastomeric Compositions*). Moscow: Akademkniga; 2006. 332 p. (in Russ.). ISBN 5-94628-296-4
16. López-Manchado M.A., Arroyo M., Herrero B., Biagiotti J. Vulcanization kinetics of natural rubber-organoclay nanocomposites. *J. Appl. Polym. Sci*. 2003;89(1):1–15. https://doi.org/10.1002/app.12082
17. Andreeva I.N., Veselovskaya E.V., Nalivaiko E.I., *et al*. *Sverkhvysokomolekulyarnyi polietilen vysokoi plotnosti* (*Ultra-High Molecular Weight Polyethylene*). Leningrad: Khimiya; 1982. 80 p. (in Russ.).
18. Zuev Yu.S. Resistance of rubber to aggressive influences. Data from recent years. Part 2. *Kauchuk i Rezina.* 2000;1:36–42 (in Russ.).
19. Alifanov E.V., Chaykun A.M., Venediktova M.A., Naumov I.S. Features of rubber formulations based on ethylene-propylene rubbers and their use in special-purpose products. *Aviatsionnye materialy i tekhnologii = Aviation Materials and Technologies*. 2015;35(2):51–55 (in Russ.). http://doi.org/10.18577/2071-9140-2015-0-2-51-55
15. Новаков И.А., Вольфсон С.И., Новопольцева О.М., Кракшин М.А. *Реологические и вулканизационные свойства эластомерных композиций*. М.: ИКЦ «Академкнига»; 2006. 332 с. ISBN 5-94628-296-4
16. López-Manchado M.A., Arroyo M., Herrero B., Biagiotti J. Vulcanization kinetics of natural rubber-organoclay nanocomposites. *J. Appl. Polym. Sci*. 2003;89(1):1–15. https://doi.org/10.1002/app.12082
17. Андреева И.Н., Веселовская Е.В., Наливайко Е.И. и др. *Сверхвысокомолекулярный полиэтилен высокой плотности*. Л.: Химия; 1982. 80 с.
18. Зуев Ю.С. Стойкость резин к агрессивным воздействиям. Данные последних лет. Часть 2. *Каучук и резина*. 2000;1:36–42.
19. Алифанов Е.В., Чайкун А.М., Венедиктова М.А., Наумов И.С. Особенности рецептур резин на основе этиленпропиленовых каучуков и их применение в изделиях специального назначения. *Авиационные материалы и технологии*. 2015;35(2):51–55. http://doi.org/10.18577/2071-9140-2015-0-2-51-55

About the authors

Marina D. Sokolova, Dr. Sci. (Eng.), Director of the Institute of Oil and Gas Problems of the Siberian Branch of the Russian Academy of Sciences, Subdivision of the Federal Research Center "The Yakut Scientific Center of the Siberian Branch of the RAS" (2, Petrovskogo ul., Yakutsk, 677007, Russia). E-mail: marsokol@mail.ru. Scopus Author ID 56896257700, ResearcherID A-5266-2014, RSCI SPIN-code 7603-7126, https://orcid.org/0000-0003-2306-5870

Anna R. Khaldeeva, Junior Researcher, Materials Science Laboratory, Institute of Oil and Gas Problems of the Siberian Branch of the Russian Academy of Sciences, Subdivision of the Federal Research Center "The Yakut Scientific Center of the Siberian Branch of the RAS" (20, Avtodorozhnaya ul., Yakutsk, 677021, Russia). E-mail: haldeeva-anna@mail.ru. Scopus Author ID 56543791200, ResearcherID F-3304-2017, RSCI SPIN-code 9794-1948, https://orcid.org/0000-0001-5639-3817

Maria L. Davydova, Cand. Sci. (Eng.), Leading Researcher, Materials Science Laboratory, Institute of Oil and Gas Problems of the Siberian Branch of the Russian Academy of Sciences, Subdivision of the Federal Research Center "The Yakut Scientific Center of the Siberian Branch of the RAS" (20, Avtodorozhnaya ul., Yakutsk, 677021, Russia). E-mail: davmlar@mail.ru. Scopus Author ID 54418553900, ResearcherID A-5434-2017, RSCI SPIN-code 9484-7082, https://orcid.org/0000-0003-2252-2515

Aitalina F. Fedorova, Cand. Sci. (Eng.), Leading Researcher, Materials Science Laboratory, Institute of Oil and Gas Problems of the Siberian Branch of the Russian Academy of Sciences, Subdivision of the Federal Research Center "The Yakut Scientific Center of the Siberian Branch of the RAS" (20, Avtodorozhnaya ul., Yakutsk, 677021, Russia). E-mail: faitalina@mail.ru. Scopus Author ID 15839740800, ResearcherID F-8834-2017, RSCI SPIN-code 4814-9708, https://orcid.org/0000-0001-6763-5746

Nikolay V. Shadrinov, Cand. Sci. (Eng.), Acting Deputy Director for Scientific Work, Institute of Oil and Gas Problems of the Siberian Branch of the Russian Academy of Sciences, Subdivision of the Federal Research Center "The Yakut Scientific Center of the Siberian Branch of the RAS" (20, Avtodorozhnaya ul., Yakutsk, 677021, Russia). E-mail: nshadrinov@gmail.com. Scopus Author ID 55978832000, ResearcherID A-6417-2014, RSCI SPIN-code 9747-4208, https://orcid.org/0000-0002-2694-9615

Об авторах

Соколова Марина Дмитриевна, д.т.н., директор Института проблем нефти и газа Сибирского отделения Российской академии наук, обособленное подразделение ФГБУН Федеральный исследовательский центр «Якутский научный центр СО РАН» (ИПНГ СО РАН) (677007, Россия, Якутск, ул. Петровского, д. 2). E-mail: marsokol@mail.ru. Scopus Author ID 56896257700, ResearcherID A-5266-2014, SPIN-код РИНЦ 7603-7126, https://orcid.org/0000-0003-2306-5870

Халдеева Анна Романовна, младший научный сотрудник, лаборатория материаловедения, Институт проблем нефти и газа Сибирского отделения Российской академии наук, обособленное подразделение ФГБУН Федеральный исследовательский центр «Якутский научный центр СО РАН» (ИПНГ СО РАН) (677021, Россия, Якутск, ул. Автодорожная, д. 20). E-mail: haldeeva-anna@mail.ru. Scopus Author ID 56543791200, ResearcherID F-3304-2017, SPIN-код РИНЦ 9794-1948, https://orcid.org/0000-0001-5639-3817

Давыдова Мария Ларионовна, к.т.н., ведущий научный сотрудник, лаборатория материаловедения, Институт проблем нефти и газа Сибирского отделения Российской академии наук, обособленное подразделение ФГБУН Федеральный исследовательский центр «Якутский научный центр СО РАН» (ИПНГ СО РАН) (677021, Россия, Якутск, ул. Автодорожная, д. 20). E-mail: davmlar@mail.ru. Scopus Author ID 54418553900, ResearcherID A-5434-2017, SPIN-код РИНЦ 9484-7082, https://orcid.org/0000-0003-2252-2515

Федорова Айталина Федоровна, к.т.н., ведущий научный сотрудник, лаборатория материаловедения, Институт проблем нефти и газа Сибирского отделения Российской академии наук, обособленное подразделение ФГБУН Федеральный исследовательский центр «Якутский научный центр СО РАН» (ИПНГ СО РАН) (677021, Россия, Якутск, ул. Автодорожная, д. 20). E-mail: faitalina@mail.ru. Scopus Author ID 15839740800, ResearcherID F-8834-2017, SPIN-код РИНЦ 4814-9708, https://orcid.org/0000-0001-6763-5746

Шадринов Николай Викторович, к.т.н., и.о. заместителя директора по научной работе Института проблем нефти и газа Сибирского отделения Российской академии наук, обособленное подразделение ФГБУН Федеральный исследовательский центр «Якутский научный центр СО РАН» (ИПНГ СО РАН) (677021, Россия, Якутск, ул. Автодорожная, д. 20). E-mail: nshadrinov@gmail.com. Scopus Author ID 55978832000, Researcher ID A-6417-2014, SPIN-код РИНЦ 9747-4208, https://orcid.org/0000-0002-2694-9615

Translated from Russian into English by N. Isaeva
Edited for English language and spelling by Thomas A. Beavitt

Tonkie Khimicheskie Tekhnologii = Fine Chemical Technologies.
2024;19(6):547–554 ISSN 2686-7575 (Online)

UDC 621.762.2:681.5.013:549.76+546.763
https://doi.org/10.32362/2410-6593-2024-19-6-547-554
EDN WTSOXP

CC BY

RESEARCH ARTICLE

Highly dispersed chromium(III) molybdate powders obtained by solid phase synthesis

Marina N. Miroshnichenko✉, Valery N. Kolosov

Tananaev Institute of Chemistry – Subdivision of the Federal Research Center "Kola Science Center of the Russian Academy of Sciences", Apatity, 184209 Russia

✉ *Corresponding author, e-mail: m.miroshnichenko@ksc.ru*

Abstract

Objectives. To obtain highly dispersed powders of chromium(III) molybdate $Cr_2(MoO_4)_3$ by solid phase synthesis and to study their porous structure.

Methods. After stirring in water, a mixture of Cr_2O_3 and MoO_3 oxide powders was dried in air and subjected to heat treatment in the temperature range of 600–800°C. After heat treatment, the products were identified by X-ray phase and sedimentation analysis. The specific surface area was measured using the Brunauer–Emmett–Teller static adsorption method. Porosity parameters were measured using the Barrett–Joyner–Halenda (BJH) method.

Results. The Gibbs free energy ΔG of the reaction between chromium and molybdenum oxides was calculated and it was shown that the process is characterized by a significant negative value of ΔG. Concurrently, the Gibbs energy exhibits a relatively weak dependence on temperature. The highly dispersed chromium(III) molybdate powders with specific surface area of 15.3–29.7 $m^2 \cdot g^{-1}$ obtained in this way were pure according to X-ray diffraction analysis. A study of the volume, diameter, and pore size distribution was conducted through the utilization of nitrogen adsorption–desorption isotherms in accordance with the BJH model.

Conclusions. It was demonstrated that $Cr_2(MoO_4)_3$ powders possess a mesoporous structure and are distinguished by a bimodal pore system comprising small pores with a diameter of 2–3 nm and larger pores with a diameter ranging from 15 to 30 nm.

Keywords

solid-phase synthesis, powder, oxide, chromium, molybdate, pores, specific surface area

Submitted: 11.09.2024
Revised: 18.09.2024
Accepted: 22.10.2024

For citation

Miroshnichenko M.N., Kolosov V.N. Highly dispersed chromium(III) molybdate powders obtained by solid phase synthesis. *Tonk. Khim. Tekhnol. = Fine Chem. Technol*. 2024;19(6):547–554. https://doi.org/10.32362/2410-6593-2024-19-6-547-554

© M.N. Miroshnichenko, V.N. Kolosov, 2024

НАУЧНАЯ СТАТЬЯ

Высокодисперсные порошки молибдата хрома(III), полученные твердофазным синтезом

М.Н. Мирошниченко✉, В.Н. Колосов

Институт химии и технологии редких элементов и минерального сырья им. И.В.Тананаева – обособленное подразделение Федерального государственного бюджетного учреждения науки Федерального исследовательского центра «Кольский научный центр Российской академии наук», Апатиты, 184209 Россия

✉ *Автор для переписки, e-mail: m.miroshnichenko@ksc.ru*

Аннотация

Цели. Получить высокодисперсные порошки молибдата хрома(III) $Cr_2(MoO_4)_3$твердофазным синтезом и исследовать их пористую структуру.

Методы. Смесь порошков оксидов Cr_2O_3 и MoO_3 после перемешивания в воде просушивали на воздухе и подвергали термообработке в температурном интервале 600–800°C. После термообработки продукты идентифицировали методами рентгенофазового и седиментационного анализа. Величину удельной поверхности измеряли адсорбционным статическим методом Брунауэра–Эммета–Теллера, а параметры пористости — методом Баррета–Джойнера–Халенды (BJH, Barrett–Joyner–Halenda).

Результаты. Рассчитана свободная энергия Гиббса ΔG реакции между оксидами хрома(III) и молибдена(VI). Показано, что процесс характеризуется значительной отрицательной величиной ΔG. При этом энергия Гиббса слабо зависит от температуры. Получены чистые по данным рентгеновского анализа высокодисперсные порошки молибдата хрома(III) с удельной поверхностью 15.3–29.7 $м^2 \cdot г^{-1}$. С использованием изотерм адсорбции–десорбции азота при помощи модели BJH исследованы объем, диаметр и распределение пор по размерам.

Выводы. Показано, что порошки $Cr_2(MoO_4)_3$ имеют мезопористую структуру и характеризуются бимодальной системой пор, состоящей из небольших пор с размерами 2–3 нм и более крупных пор с размерами от 15 до 30 нм.

Ключевые слова

твердофазный синтез, порошок, оксид, хром, молибдат, поры, удельная поверхность

Поступила: 11.09.2024
Доработана: 18.09.2024
Принята в печать: 22.10.2024

Для цитирования

Мирошниченко М.Н., Колосов В.Н. Высокодисперсные порошки молибдата хрома(III), полученные твердофазным синтезом. *Тонкие химические технологии*. 2024;19(6):547–554. https://doi.org/10.32362/2410-6593-2024-19-6-547-554

INTRODUCTION

Chromium(III) molybdenum $Cr_2(MoO_4)_3$ belongs to the family of chemical compounds with the general formula $A_2M_3O_{12}$, where A is a trivalent transition metal or lanthanide, and M is molybdenum or tungsten [1–6]. These compounds possess distinctive structural, thermal, magnetic, and electrical characteristics. These materials are distinguished by a phase transition from a low-temperature monoclinic structure ($P2_1/a$) to a high-temperature orthorhombic structure ($Pbcn$). Both structures are microporous, forming open interstitial cationless frameworks consisting of AO_6 octahedra and MO_4 tetrahedra connected by vertices. The AO_6 octahedra are connected to the MO_4 tetrahedra by a common oxygen atom at each vertex. In orthorhombic modification, compounds $A_2M_3O_{12}$ exhibit negative thermal expansion, the causes of which have not yet been precisely determined [7]. Materials exhibiting negative thermal expansion have significant potential for use in the creation of composite materials with an adjustable coefficient of thermal expansion [8]. Based on the compounds $A_2M_3O_{12}$, functional materials can be created for various purposes. In particular, chromium(III) molybdate is a ferrimagnet [9] and is characterized by two different conduction mechanisms [10]. Below the structural phase transition temperature (about 650 K) $Cr_2(MoO_4)_3$ is a *p*-type semiconductor, while above it is an *n*-type semiconductor. Additionally, chromium(III) molybdate displays catalytic activity and can be employed as a catalyst in alcohol oxidation, *n*-octane dehydrogenation, and other chemical reactions [11–14].

In order to obtain $Cr_2(MoO_4)_3$, the following are used: mechanosynthesis [15, 16]; solid-phase synthesis [17]; sol–gel method [9], co-precipitation of a soluble chromium salt and molybdenum acid [18]; and co-decomposition of a mixture of bichromate and ammonium paramolybdate

followed by calcination of the resulting product [19]. The techniques currently available possess certain disadvantages. These include the length of time required for the process, the necessity for maintaining a constant pH value of the reagent solutions, and the occurrence of hydrolytic processes in the solutions themselves. Furthermore, the resulting chromium(III) molybdenum powders exhibit an inadequate specific surface area. For example, the surface of powders obtained using mechanosynthesis is 1.3–3.6 $m^2 \cdot g^{-1}$ [15].

The objective of this study is to synthesize highly dispersed chromium(III) molybdate powders by means of a solid-phase approach with a view to investigating their porous structure.

MATERIALS AND METHODS

Oxides of MoO_3 (pure, TU 6-094471-77, *Khimreaktivnab*, Russia) and Cr_2O_3 were used as precursors. Chromium(III) oxide was obtained by calcination of ammonium dichromate $(NH_4)_2Cr_2O_7$ (chemically pure, GOST 3763-76[1], *Khimreaktivnab)*. Cr_2O_3 and MoO_3 oxide powders were weighed in accordance with the stoichiometric ratio of chromium and molybdenum in the compound $Cr_2(MoO_4)_3$. The oxides were then mixed in water in a solid/liquid phase ratio = 1 : 5 using an overhead stirrer RW16basic (*IKA*, Germany) for 3 h. The rotation speed of the mixer is 320 min^{-1}. Following the mixing process, the mixture was subjected to drying in air at a temperature range of 80–85°C. Subsequently the mixture underwent heat treatment in a laboratory-based muffle furnace (*Sikron*, Russia) at an initial temperature of 600°C for a period of 5 h. This was followed by a repeated heat treatment in the range of 700–800°C for a further 6 h.

Phase analysis of the reagents and the products obtained was determined using a *Shimadzu* XRD-6000 diffractometer (Japan) (CuK_α-radiation) using the ICCD PDF-2 diffractometric database[2]. The average particle size D of $Cr_2(MoO_4)_3$ powder was estimated under the assumption that they have a spherical shape, according to the formula:

$$D = \frac{6}{S_{BET} \cdot \rho}, \quad (1)$$

wherein S_{BET} is the specific surface area of the powder, ρ is the density of $Cr_2(MoO_4)_3$. The specific surface area was measured by means of the Brunauer–Emmett–Teller (BET) adsorption static method. The porosity parameters were measured by the Barrett–Joyner–Halenda method on a Micrometrics TriStar II 3020 device (*Micrometrics Instrument Corporation*, USA) using nitrogen adsorption–desorption isotherms. The particle size distribution of the powders was analyzed on a photometric sedimentometer FSH-6K (*Labnauchpribor*, Russia).

RESULTS AND DISCUSSION

The synthesis of chromium(III) molybdate is based on a solid phase reaction between oxides of the corresponding metals:

$$Cr_2O_3\,(solid) + 3MoO_3\,(solid) = Cr_2(MoO_4)_3\,(solid) \quad (2)$$

The Gibbs free energy ΔG of the reaction (2) was calculated as a function of temperature (Fig. 1).

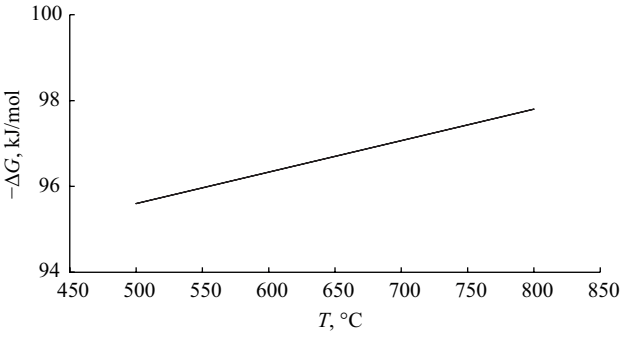


Fig. 1. Gibbs free energy ΔG as a function of the reaction temperature for the formation of chromium(III) molybdate

The calculation was carried out using the entropy method, while considering the aggregate state of the reaction participants. The necessary thermodynamic values of chromium oxides and molybdenum used in the calculations were taken from [20, 21]. The reaction (2) is energetically advantageous for synthesis within the specified temperature range. In this case, the Gibbs energy is observed to exhibit a relatively weak dependence on temperature. The chromium(III) molybdate powders, which were found to be of a high degree of purity according to X-ray phase analysis, were obtained as a result of double sintering of the charge. The initial charge and reaction products are displayed in Fig. 2, together with their respective diffractograms, subjected to heat treatment.

The research yielded chromium(III) molybdate powders with a specific surface area of 15.3–29.6 $m^2 \cdot g^{-1}$. Figure 3 illustrates the typical integral particle size distribution observed in powder samples.

[1] GOST 3763-76. State Standard of the USSR. Reagents. Ammonium bichromate. Specifications. Moscow: IPK Izdatelstvo Standartov; 1998.

[2] https://www.icdd.com/pdf-2/. Accessed November 22, 2022.

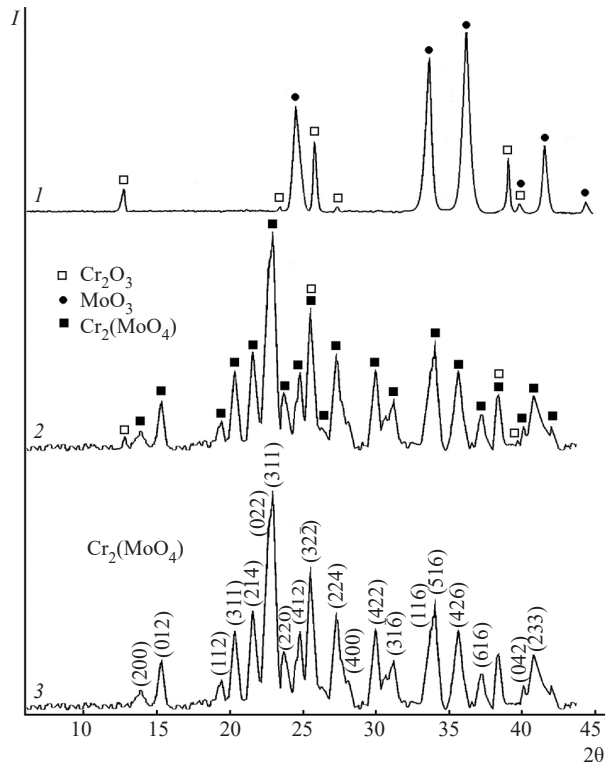


Fig. 2. Initial mixture of metal oxides (*1*) and the resulting diffractogram after heat treatment (*2*, *3*). Sintering conditions: (*2*) 600°C, 5 h + 800°C, 4 h; (*3*) 600°C, 5 h + 800°C, 6 h

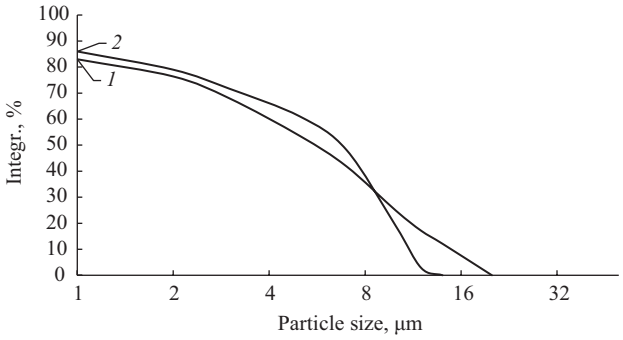


Fig. 3. Integral particle size distribution of $Cr_2(MoO_4)_3$ powders. Specific surface area of powders: (*1*) 15.3 $m^2 \cdot g^{-1}$, (*2*) 29.7 $m^2 \cdot g^{-1}$

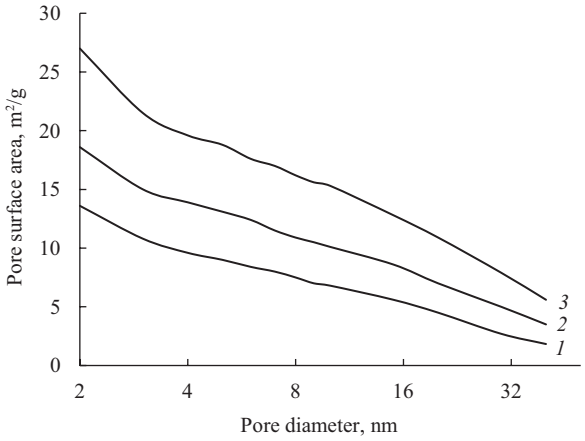


Fig. 4. Dependencies of the total pore surface on their average diameter for $Cr_2(MoO_4)_3$ powders. Specific surface area of powders: (*1*) 15.3, (*2*) 20.3, (*3*) 29.7 $m^2 \cdot g^{-1}$

Figure 3 illustrates that, despite the considerable discrepancy in the value of specific surface area, the powder samples exhibit minimal variation in their particle size distribution. The majority of particles, comprising approximately 70% of the total, are smaller than 9 μm, with a further 25% less than 2 μm in size. According to calculations using formula (1), the average particle size of $Cr_2(MoO_4)_3$ is in the range of 60–115 nm. It can thus be surmised that, in view of the specific surface area of the powders, the particles of the chromium molybdenum powder are to a considerable extent agglomerated. The process of agglomeration results in the formation of a porous material.

Figure 4 illustrates the relationship between the total surface area of the pores and their average diameter.

The total surface area of the powders obtained is approximately equivalent to the total surface area of the pores. Therefore, the outer surface area of the chromium(III) molybdate particles is insignificant in comparison to the developed inner porous surface area, which constitutes the majority of the powder's surface area. The type of adsorption–desorption isotherms of $Cr_2(MoO_4)_3$ powders is shown in Fig. 5. The isotherms observed for the powders can be classified as type IV according to the IUPAC classification, with the presence of H3 hysteresis loops. Isotherms of this nature are typical of mesoporous substances, characterized by disordered aggregates forming slit-shaped pores [22, 23]. With an increase in the specific surface area of powders from 15.3 to 29.6 $m^2 \cdot g^{-1}$, the adsorption–desorption isotherms show an increase in the amount of adsorbed nitrogen (Fig. 5). This is a consequence of the increased porosity of the material, which allows for greater permeability.

As illustrated in Fig. 6, the pore size distribution of chromium(III) molybdenum powders exhibits a bimodal character in the mesoporous region. The subject of such materials is currently attracting a growing amount of attention. When employed in the context of catalysts, these materials have been demonstrated to effectively reduce the diffusion resistance and enhance the catalytic efficiency of heterogeneous reactions [24–26].

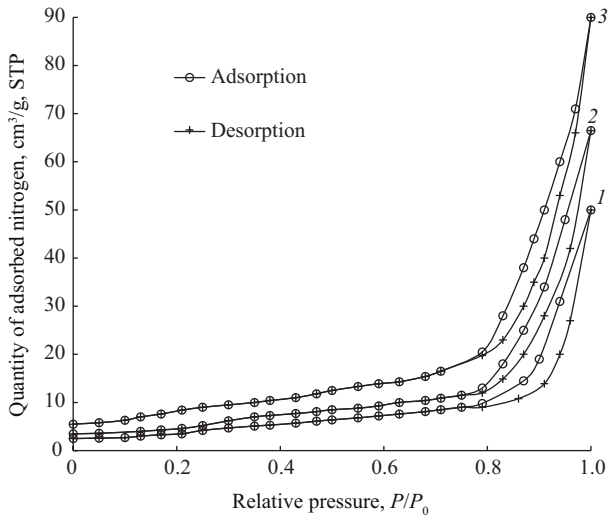


Fig. 5. Nitrogen adsorption–desorption isotherms of $Cr_2(MoO_4)_3$ powders
(STP is the standard temperature of 273.15 K (0°C, 32°F) and pressure of exactly 105 Pa (1 atm, 1 bar)).
Specific surface area of powders:
(*1*) 15.3,
(*2*) 20.3,
(*3*) 29.7 $m^2 \cdot g^{-1}$

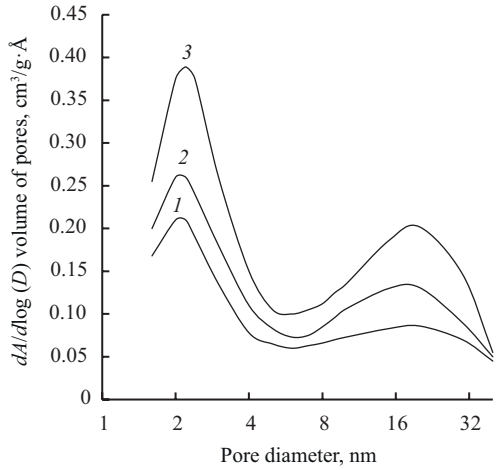


Fig. 6. Pore distribution in $Cr_2(MoO_4)_3$ powders.
Specific surface area of powders:
(*1*) 15.3,
(*2*) 20.3,
(*3*) 29.7 $m^2 \cdot g^{-1}$

According to [27], the bimodal pore distribution is due to the presence of solid aggregates in powders, in which there are two types of pores. One category of pores is of a smaller intra-aggregate size, while the other is of a larger inter-aggregate size. In accordance with this definition, the intraaggregate pores of the obtained chromium(III) molybdate powders have a diameter of 2–3 nm, while the interaggregate pores exhibit a broader distribution, with a diameter ranging from 15 to 30 nm. Modifying the heat treatment parameters of the initial metal oxide mixture allows for the alteration of the pore density within the resulting powder. With an increase in the specific surface area of chromium(III) molybdate powders, the pore volume of both pore types increases (Fig. 6).

CONCLUSIONS

A solid-phase method was employed at temperatures between 600 and 800°C to synthesize chromium(III) molybdenum powders with a high degree of dispersion and a specific surface area of 15.3 to 29.7 $m^2 \cdot g^{-1}$, as determined by X-ray analysis. The pore distribution of powders is bimodal in nature. Intraaggregate pores are 2–3 nm, while interaggregate pores are at the level of 15–30 nm. The resulting powders can be used as precursors in the creation of catalysts.

Authors' contributions

M.N. Miroshnichenko—synthesis of compounds, writing the text of the article.

V.N. Kolosov—processing experimental results, writing the text of the article.

The authors declare no conflicts of interest.

REFERENCES

1. Tyagi A.K., Achary S.N., Mathews M.D. Phase Transition and Negative Thermal Expansion in $A_2(MoO_4)_3$ System (A=Fe^{3+}, Cr^{3+} and Al^{3+}). *J. Alloys Compd*. 2002;339(1–2):1377–1383. https://doi.org/10.1016/S0925-8388(01)02003-5
2. Liu J., Sharma N. Thermal Evolution and Phase Transitions in Electrochemically Activated $Sc_2(MoO_4)_3$. *Inorg. Chem.* 2019;58(9):9964–9973. https://doi.org/10.1021/acs.inorgchem.9b01116
3. Pudge G.J.F., Hutchings G.J., Kondrat S.A., Morrison K., Perkins E.F., Rushbya A.V., Bartley J.K. Iron molybdate catalysts synthesised via dicarboxylate decomposition for the partial oxidation of methanol to formaldehyde. *Catal. Sci. Technol.* 2022;12(14):4552–4560. http://doi.org/10.1039/D2CY00699E
4. Dias A.P.S., Rijo B., Kiennemann A., Portela M.F. Methanol oxidation over iron molybdate catalysts. Main and side reactions kinetics. *Appl. Catal. A Gen*. 2023;658(5):119118. https://doi.org/10.1016/j.apcata.2023.119118
5. Gurusamy L., Karuppasamy L., Anandan S., Liu C.-H., Wu J.J. Recent advances on metal molybdate-based electrode materials for supercapacitor application. *J. Energy Storage*. 2024;79(2):110122. https://doi.org/10.1016/j.est.2023.110122
6. El-Aryan Y.F., Melhi S. Adsorption Study of Eriochrome Black T Dye on Polyacrylonitrile Chromium molybdate Composite. *Russ. J. Appl. Chem*. 2024. https://doi.org/10.1134/S1070427224020125
7. Miller W., Smith C.W., Mackenzie D.S., Evans K.E. Negative thermal expansion: a review. *J. Mater. Sci.* 2009;44(20):5441–5451. https://doi.org/10.1007/s10853-009-3692-4
8. Zhang Z., Sun W., Zheng Q., Liu H., Zhou M., Wang W., Chen X. Tuning the Phase Transition Temperature of $Cr_2(MoO_4)_3$ by A-site Substitution of Scandium. *Ceram. Int.* 2018;44(18):22165–22171. https://doi.org/10.1016/j.ceramint.2018.08.329
9. Battle P.D., Cheetham A.K., Harrison W.T.A., Pollard N.J., Faber J. The Structure and Magnetic Properties of Chromium(III) Molybdate. *J. Solid State. Chem*. 1985;58(2):221–225. https://doi.org/10.1016/0022-4596(85)90238-5
10. Ansari T.H., Yadava Y.P. Electrical Conduction in Polycrystalline Chromium Molybdate. *Mater. Lett.* 1990;9(11):469–473. https://doi.org/10.1016/0167-577x(90)90120-b
11. Popov T.S., Popov B.I., Bibin V.N., Bliznakov G.M., Boreskov G.K. Catalytic Properties of Chromium-Molybdenum Oxide Catalysts in Methanol Oxidation. React. *Kinet. Catal. Lett*. 1975;3(2):169–175. https://doi.org/10.1007/bf02187510
12. Oudghiri-Hassani H. Synthesis, Characterization and Application of Chromium Molybdate for Oxidation of Methylene Blue Dye. *J. Mater. Environ. Sci.* 2018;9(2):1051–1057. https://doi.org/10.26872/jmes.2018.9.3,117
13. Yadagiri M., Ramakrishna S., Ravi G., Suresh P., Sreenu K., Jaya-Prakash D., Vithal M. Preparation, Characterization and Photocatalytic Studies of $Cr_2(MoO_4)_3$ and Nitrogen-Doped $Cr_2(MoO_4)_3$. *Chem. Chem. Technol*. 2015;9(4):391–399. https://doi.org/10.23939/chcht09.04.391
14. Bandaru H., Mahomed A.S., Singh S., Friedrich H.B. The Effect of Varying the Metal Ratio in a Chromium Molybdate Catalysts for the Oxidative Dehydrogenation of *n*-octane. *Mol. Catal.* 2018;460(9):74–82. https://doi.org/10.1016/j.mcat.2018.09.017
15. Klissurski D., Mancheva M., Iordanova R., Kunev B. Synthesis of $Cr_2(MoO_4)_3$ from Mechanically Activated Precursors. *Khimiya v interesakh ustoichivogo razvitiya = Chemistry for Sustainable Development*. 2005;13(2):229–232(in Russ.).

СПИСОК ЛИТЕРАТУРЫ

1. Tyagi A.K., Achary S.N., Mathews M.D. Phase Transition and Negative Thermal Expansion in $A_2(MoO_4)_3$ System (A=Fe^{3+}, Cr^{3+} and Al^{3+}). *J. Alloys Compd*. 2002;339(1–2):1377–1383. https://doi.org/10.1016/S0925-8388(01)02003-5
2. Liu J., Sharma N. Thermal Evolution and Phase Transitions in Electrochemically Activated $Sc_2(MoO_4)_3$. *Inorg. Chem.* 2019;58(9):9964–9973. https://doi.org/10.1021/acs.inorgchem.9b01116
3. Pudge G.J.F., Hutchings G.J., Kondrat S.A., Morrison K., Perkins E.F., Rushbya A.V., Bartley J.K. Iron molybdate catalysts synthesised via dicarboxylate decomposition for the partial oxidation of methanol to formaldehyde. *Catal. Sci. Technol*. 2022;12(14):4552–4560. http://doi.org/10.1039/D2CY00699E
4. Dias A.P.S., Rijo B., Kiennemann A., Portela M.F. Methanol oxidation over iron molybdate catalysts. Main and side reactions kinetics. *Appl. Catal. A Gen*. 2023;658(5):119118. https://doi.org/10.1016/j.apcata.2023.119118
5. Gurusamy L., Karuppasamy L., Anandan S., Liu C.-H., Wu J.J. Recent advances on metal molybdate-based electrode materials for supercapacitor application. *J. Energy Storage*. 2024;79(2):110122. https://doi.org/10.1016/j.est.2023.110122
6. El-Aryan Y.F., Melhi S. Adsorption Study of Eriochrome Black T Dye on Polyacrylonitrile Chromium molybdate Composite. *Russ. J. Appl. Chem*. 2024. https://doi.org/10.1134/S1070427224020125
7. Miller W., Smith C.W., Mackenzie D.S., Evans K.E. Negative thermal expansion: a review. *J. Mater. Sci.* 2009;44(20):5441–5451. https://doi.org/10.1007/s10853-009-3692-4
8. Zhang Z., Sun W., Zheng Q., Liu H., Zhou M., Wang W., Chen X. Tuning the Phase Transition Temperature of $Cr_2(MoO_4)_3$ by A-site Substitution of Scandium. *Ceram. Int.* 2018;44(18):22165–22171. https://doi.org/10.1016/j.ceramint.2018.08.329
9. Battle P.D., Cheetham A.K., Harrison W.T.A., Pollard N.J., Faber J. The Structure and Magnetic Properties of Chromium(III) Molybdate. *J. Solid State. Chem*. 1985;58(2):221–225. https://doi.org/10.1016/0022-4596(85)90238-5
10. Ansari T.H., Yadava Y.P. Electrical Conduction in Polycrystalline Chromium Molybdate. *Mater. Lett.* 1990;9(11):469–473. https://doi.org/10.1016/0167-577x(90)90120-b
11. Popov T.S., Popov B.I., Bibin V.N., Bliznakov G.M., Boreskov G.K. Catalytic Properties of Chromium-Molybdenum Oxide Catalysts in Methanol Oxidation. React. *Kinet. Catal. Lett*. 1975;3(2):169–175. https://doi.org/10.1007/bf02187510
12. Oudghiri-Hassani H. Synthesis, Characterization and Application of Chromium Molybdate for Oxidation of Methylene Blue Dye. *J. Mater. Environ. Sci.* 2018;9(2):1051–1057. https://doi.org/10.26872/jmes.2018.9.3,117
13. Yadagiri M., Ramakrishna S., Ravi G., Suresh P., Sreenu K., Jaya-Prakash D., Vithal M. Preparation, Characterization and Photocatalytic Studies of $Cr_2(MoO_4)_3$ and Nitrogen-Doped $Cr_2(MoO_4)_3$. *Chem. Chem. Technol*. 2015;9(4):391–399. https://doi.org/10.23939/chcht09.04.391
14. Bandaru H., Mahomed A.S., Singh S., Friedrich H.B. The Effect of Varying the Metal Ratio in a Chromium Molybdate Catalysts for the Oxidative Dehydrogenation of *n*-octane. *Mol. Catal.* 2018;460(9):74–82. https://doi.org/10.1016/j.mcat.2018.09.017
15. Klissurski D., Mancheva M., Iordanova R., Kunev B. Synthesis of $Cr_2(MoO_4)_3$ from Mechanically Activated Precursors. *Химия в интересах устойчивого развития.* 2005;13(2):229–232.

16. Batanov A.A., Rumyantsev R.N., Goryanskaya V.A., Il'in A.A., Il'in A.P. Mechanochemical synthesis of chromium(III) molybdates on the basis of various precursors. *Vestnik Tverskogo Gosudarstvennogo Universiteta. Seriya: Khimiya = Herald of Tver State University. Series: Chemistry*. 2020;1(39):96–109 (in Russ.). https://doi.org/10.26456/vtchem2020.1.11
17. Shurdumov G.K., Tlikhuryaeva M.M., Kardanova Yu.L., Shurdumov B.K. Solid-phase synthesis of highly dispersed chromium(III) molybdate based on the Cr_2SO_4-Na_2CO_3-MoO_3 system. *Khimiya v interesakh ustoichivogo razvitiya = Chemistry for Sustainable Development*. 2016;24:805–810 (in Russ.). https://doi.org/10.15372/KhUR20160611
18. Plyasova L.M., Kefeli L.M. X-ray study of chromium and aluminum molybdates. *Izvestiya AN SSSR. Neorganicheskie Materialy*. 1967;3(5):906–908 (in Russ.).
19. Butukhanov V.D., Get'man E.I., Mokhosoev M.V. Interaction of lithium molybdate with chromium molybdate. *Zhurnal Neorganicheskoi Khimii.* 1972;17(4):1169–1171 (in Russ.).
20. Binnewies M., Mike E. *Thermochemical Data of Elements and Compounds*. Wenham: Wiley-VCH Verlag GmbH; 2002. 936 p. https://doi.org/10.1002/9783527618347
21. Tamm M.E., Tretyakov Yu.D. *Neorganicheskaya khimiya* (*Inorganic Chemistry*): in 3 v. Moscow: Akademiya; 2004. V.1. 240 p. (in Russ.).
22. Sing K.S.W. Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity (Recommendations 1984). *Pure Appl. Chem*. 1985;57(4):603–619. https://doi.org/10.1351/pac198557040603
23. Thommes M., Kaneko K., Neimark A.V., Olivier J.P., Rodriguez-Reinoso F., Rouquerol J., Sing K.S.W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure Appl. Chem*. 2015;87(9):1051–1069. https://doi.org/10.1515/pac-2014-1117
24. Yu J., Wang G., Cheng B., Zhou M. Effects of Hydrothermal Temperature and Time on the Photocatalytic Activity and Microstructures of Bimodal Mesoporous TiO_2 Powders. *Appl. Catal. B: Environmental*. 2007;69(3–4):171–180. https://doi.org/10.1016/j.apcatb.2006.06.022
25. Yang L., Guo M., Zhang F., Jing Y., Wang Y., Luo G. Controllable Preparation of γ-Alumina Nanoparticles with Bimodal Pore Size Distribution in Membrane Dispersion Microreactor. *Particuology*. 2018;41(12):1–10. https://doi.org/10.1016/j.partic.2018.04.001
26. Fuentes-Quezada E., de la Llave E., Halac E., Jobbágy M., Viva F.A., Bruno M.M., Corti H.R. Bimodal Mesoporous Hard Carbons from Stabilized Resorcinol-Formaldehyde Resin and Silica Template with Enhanced Adsorption Capacity. *Chem. Eng. J.* 2019;360(3):631–644. https://doi.org/10.1016/j.cej.2018.11.235
27. Kumar K.-N.P., Kumar J., Keizer K. Effect of Peptization on Densification and Phase-Transformation Behavior of Sol–Gel-Derived Nanostructured Titania. *J. Am. Ceram. Soc*. 1994;77(5):1396–1400. https://doi.org/10.1111/j.1151-2916.1994.tb05426.x

16. Батанов А.А., Румянцев Р.Н., Горянская В.А., Ильин А.А., Ильин А.П. Механохимический синтез молибдатов хрома(III) на основе различных прекурсоров. *Вестник ТвГУ. Серия: Химия*. 2020;1(39):96–109. https://doi.org/10.26456/vtchem2020.1.11
17. Шурдумов Г.К., Тлихуряева М.М., Карданова Ю.Л., Шурдумов Б.К. Твердофазный синтез высокодисперсного молибдата хрома(III) на основе системы Cr_2SO_4-Na_2CO_3-MoO_3. *Химия в интересах устойчивого развития*. 2016;24:805–810. https://doi.org/10.15372/KhUR20160611
18. Плясова Л.М., Кефели Л.М. Рентгенографическое исследование молибдатов хрома и алюминия. *Изв. АН СССР. Неорган. материалы*. 1967;3(5):906–908.
19. Бутуханов В.Д., Гетьман Е.И., Мохосоев М.В. Взаимодействие молибдата лития с молибдатом хрома. *Журн. неорган. химии*. 1972;17(4):1169–1171.
20. Binnewies M., Mike E. *Thermochemical Data of Elements and Compounds*. Wenham: Wiley-VCH Verlag GmbH; 2002. 936 p. https://doi.org/10.1002/9783527618347
21. Тамм М.Е., Третьяков Ю.Д. *Неорганическая химия*: в 3 т. М.: Академия; 2004. Т.1. 240 с.
22. Sing K.S.W. Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity (Recommendations 1984). *Pure Appl. Chem*. 1985;57(4):603–619. https://doi.org/10.1351/pac198557040603
23. Thommes M., Kaneko K., Neimark A.V., Olivier J.P., Rodriguez-Reinoso F., Rouquerol J., Sing K.S.W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure Appl. Chem*. 2015;87(9):1051–1069. https://doi.org/10.1515/pac-2014-1117
24. Yu J., Wang G., Cheng B., Zhou M. Effects of Hydrothermal Temperature and Time on the Photocatalytic Activity and Microstructures of Bimodal Mesoporous TiO_2 Powders. *Appl. Catal. B: Environmental*. 2007;69(3–4):171–180. https://doi.org/10.1016/j.apcatb.2006.06.022
25. Yang L., Guo M., Zhang F., Jing Y., Wang Y., Luo G. Controllable Preparation of γ-Alumina Nanoparticles with Bimodal Pore Size Distribution in Membrane Dispersion Microreactor. *Particuology*. 2018;41(12):1–10. https://doi.org/10.1016/j.partic.2018.04.001
26. Fuentes-Quezada E., de la Llave E., Halac E., Jobbágy M., Viva F.A., Bruno M.M., Corti H.R. Bimodal Mesoporous Hard Carbons from Stabilized Resorcinol-Formaldehyde Resin and Silica Template with Enhanced Adsorption Capacity. *Chem. Eng. J.* 2019;360(3):631–644. https://doi.org/10.1016/j.cej.2018.11.235
27. Kumar K.-N.P., Kumar J., Keizer K. Effect of Peptization on Densification and Phase-Transformation Behavior of Sol–Gel-Derived Nanostructured Titania. *J. Am. Ceram. Soc*. 1994;77(5):1396–1400. https://doi.org/10.1111/j.1151-2916.1994.tb05426.x

About the authors

Marina N. Miroshnichenko, Cand. Sci. (Eng.), Researcher, Tananaev Institute of Chemistry — Subdivision of the Federal Research Center "Kola Science Center of the Russian Academy of Sciences" (ICT KSC RAS) (26a, Akademgorodok, Apatity, Murmansk oblast, 184209, Russia). E-mail: m.miroshnichenko@ksc.ru. ResearcherID P-9964-2017, Scopus Author ID 8522192100, RSCI SPIN-code 7948-2708, https://orcid.org/0000-0002-5925-4561

Valery N. Kolosov, Dr. Sci. (Eng.), Chief Researcher, Tananaev Institute of Chemistry — Subdivision of the Federal Research Center "Kola Science Center of the Russian Academy of Sciences" (ICT KSC RAS) (26a, Akademgorodok, Apatity, Murmansk oblast, 184209, Russia). E-mail: v.kolosov@ksc.ru. ResearcherID Q-8446-2017, Scopus Author ID 35275498200, RSCI SPIN-code 1801-2839, https://orcid.org/0000-0002-4749-236X

Об авторах

Мирошниченко Марина Николаевна, к.т.н., научный сотрудник, Институт химии и технологии редких элементов и минерального сырья им. И.В.Тананаева – обособленное подразделение Федерального государственного бюджетного учреждения науки Федерального исследовательского центра «Кольский научный центр Российской академии наук» (ИХТРЭМС КНЦ РАН) (184209, Россия, г. Апатиты, Мурманская обл., Академгородок, д. 26а). E-mail: m.miroshnichenko@ksc.ru. ResearcherID P-9964-2017, Scopus Author ID 8522192100, SPIN-код РИНЦ 7948-2708, https://orcid.org/0000-0002-5925-4561

Колосов Валерий Николаевич, д.т.н., главный научный сотрудник, Институт химии и технологии редких элементов и минерального сырья им. И.В.Тананаева – обособленное подразделение Федерального государственного бюджетного учреждения науки Федерального исследовательского центра «Кольский научный центр Российской академии наук» (ИХТРЭМС КНЦ РАН) (184209, Россия, г. Апатиты, Мурманская обл., Академгородок, д. 26а). E-mail: v.kolosov@ksc.ru. ResearcherID Q-8446-2017, Scopus Author ID 35275498200, SPIN-код РИНЦ 1801-2839, https://orcid.org/0000-0002-4749-236X

Translated from Russian into English by N. Isaeva
Edited for English language and spelling by Dr. David Mossop

Tonkie Khimicheskie Tekhnologii = Fine Chemical Technologies.
2024;19(6):555–564 ISSN 2686-7575 (Online)

UDC 519.245, 678.7
https://doi.org/10.32362/2410-6593-2024-19-6-555-564
EDN XAITKL

CC BY

RESEARCH ARTICLE

Computer modeling of the synthesis of styrene–butadiene rubber: Influence of the feed of a chain transfer agent on the characteristics of the product

Tatiana A. Mikhailova✉, **Svetlana A. Mustafina**
Ufa University of Science and Technology, Ufa, 450076 Russia
✉ *Corresponding author, e-mail: T.A.Mihailova@yandex.ru*

Abstract

Objectives. To develop mathematical approaches and algorithms for analyzing the influence of various methods for feeding a chain transfer agent to a cascade of reactors, taking into account the choice of feed points on the characteristics of the final product of copolymerization using computer modeling.

Methods. The processes of synthesis of copolymers were mathematically modeled using a statistical approach (Monte Carlo method). The developed algorithm is based on calculating the probabilities of elementary reactions in the process under study. In the case of continuous production of the copolymer in a cascade of reactors, it must be taken into account that the residence time of each particle of the reaction mixture in the reactor is subject to a probability distribution. The algorithm models the formation of copolymer macromolecules at the particle level, permitting the average molecular characteristics of the copolymer to be calculated and its microstructure to be studied based on modeling results.

Results. The dependencies of the intrinsic viscosity on the reactor number and conversion were constructed by means of mathematical modeling. The calculation results showed satisfactory agreement with the experimental data obtained in production. The dependencies of the molecular weight distribution of the copolymer, the weight-average molecular weight, and the microheterogeneity index on the reactor number were constructed for various methods of feed of the chain transfer agent, i.e., to two and/or three points of the reactor cascade. The modeling and calculation results confirmed the influence of the method of adding the chain transfer agent to the cascade reactors on the molecular characteristics of the copolymer.

Conclusions. The analysis of the structure of the molecular units of the styrene–butadiene copolymer showed a decrease in the weight-average molecular weight of the final product and an increase in its stiffness in the case of the three-point feed of the chain transfer agent.

Keywords

copolymerization, reactor cascade, butadiene, styrene, tertiary dodecyl mercaptan, statistical modeling, Monte Carlo method, molecular weight distribution, polydispersity, microheterogeneity

Submitted: 28.06.2024
Revised: 26.07.2024
Accepted: 21.10.2024

For citation

Mikhailova T.A., Mustafina S.A. Computer modeling of the synthesis of styrene–butadiene rubber: Influence of the feed of a chain transfer agent on the characteristics of the product. *Tonk. Khim. Tekhnol. = Fine Chem. Technol*. 2024;19(6):555–564. https://doi.org/10.32362/2410-6593-2024-19-6-555-564

© T.A. Mikhailova, S.A. Mustafina, 2024

НАУЧНАЯ СТАТЬЯ

Компьютерное моделирование процесса синтеза бутадиен-стирольного каучука: влияние подачи регулятора на характеристики продукта

Т.А. Михайлова✉, С.А. Мустафина

Уфимский университет науки и технологий, Уфа, 450076 Россия

✉ *Автор для переписки, e-mail: T.A.Mihailova@yandex.ru*

Аннотация

Цели. Развитие математических подходов и алгоритмов анализа влияния различных способов подачи регулятора в каскад реакторов с учетом выбора точек подачи на характеристики конечного продукта процесса сополимеризации с применением компьютерного моделирования.

Методы. При математическом моделировании процессов синтеза сополимеров применялся статистический подход (метод Монте-Карло). Разработанный авторами алгоритм основан на вычислении вероятностей осуществления элементарных реакций исследуемого процесса. В случае непрерывного производства сополимера в каскаде реакторов необходимо учитывать, что время пребывания каждой частицы реакционной смеси в реакторе подчиняется вероятностному распределению. Реализация алгоритма позволяет имитировать образование макромолекул сополимера на уровне частиц, что дает возможность вычислять его усредненные молекулярные характеристики и исследовать микроструктуру на основе данных, полученных в результате моделирования.

Результаты. Методами математического моделирования построены зависимости характеристической вязкости от номера реактора и конверсии. Результаты расчетов показали удовлетворительное согласование с экспериментальными данными, полученными на производстве. Построены зависимости молекулярно-массового распределения сополимера, среднемассовой молекулярной массы и коэффициента микрогетерогенности от номера реактора для различных режимов подачи регулятора — в две и/или три точки каскада реакторов. Анализ результатов моделирования и расчетов подтвердил влияние способа добавления регулятора в реакторы каскада на молекулярные характеристики сополимера.

Выводы. Анализ структуры молекулярных звеньев бутадиен-стирольного сополимера показал снижение среднемассовой молекулярной массы конечного продукта и увеличение его жесткости при трехточечном режиме регулирования процесса.

Ключевые слова

сополимеризация, каскад реакторов, бутадиен, стирол,
третичный додецилмеркаптан, статистическое моделирование, метод Монте-Карло,
молекулярно-массовое распределение, полидисперсность, микрогетерогенность

Поступила: 28.06.2024
Доработана: 26.07.2024
Принята в печать: 21.10.2024

Для цитирования

Михайлова Т.А., Мустафина С.А. Компьютерное моделирование процесса синтеза бутадиен-стирольного каучука: влияние подачи регулятора на характеристики продукта. *Тонкие химические технологии*. 2024;19(6):555–564. https://doi.org/10.32362/2410-6593-2024-19-6-555-564

INTRODUCTION

In modern industry, the production of synthetic materials, in particular, rubber is one of the key industries which contribute to progress in various fields, such as the automotive industry, chemical industry, medicine, among others. However, there is an urgent need for the development, modification, and optimization of technological processes requiring many factors and parameters to be considered in their production.

Natural rubber does not have the qualities necessary for the creation of high-quality rubber products. Therefore, a wide variety of types of synthetic rubber are produced. It is synthesized under industrial conditions by polymerization/copolymerization processes [1]. The resulting product, unlike natural rubber, is resistant to environmental damage, highly elastic, and can withstand low temperatures. The material formed in the process is subsequently processed into rubber by vulcanization.

Styrene–butadiene synthetic rubber from the group of general-purpose rubbers is the most widely used in comparison with other large-tonnage rubbers. In world production, its fraction is slightly more than 30%. It is used in the production of various rubber products (car mats, hoses, shoe soles, cable insulation, etc.), with the

main area of application being the production of tires, mainly for passenger cars [2].

Synthetic rubbers based on butadiene and styrene are synthesized by free-radical styrene-butadiene copolymerization in an aqueous emulsion. This process is carried out at low temperatures (5–6°C) in a continuous mode in several reactors simultaneously combined into a cascade of 9–12 stirred-tank reactors, shown in Fig. 1, as a component of the production scheme. In this case, the flow of the reaction mixture is continuously fed into the first reactor of the cascade, and the reaction products are removed from the last reactor [3]. The described approach to carrying out the process significantly reduces the operating costs of the reactors, extends the overall service life, and ensures the stability of the technological process and, consequently, the stability of the manufactured product [4].

One of the important process parameters affecting the properties of the polymer product is the feed mode of the chain transfer agent (CTA), i.e., its quantity, feed rate, feed points, and feed time. Changing the CTA feed mode can significantly affect the molecular weight, structure, and properties of the formed product, which are directly related to its performance [5].

Mathematical modeling of polymerization and copolymerization processes plays an important role in studying their various aspects and, accordingly, their optimization [6]. Research based on constructing a mathematical model is focused on calculating the characteristics of the formed copolymer and the product obtained, as well as finding optimization modes for controlling the process parameters, and analyzing their mutual influence under industrial production conditions [7].

This work aims to study the effect of various CTA feed modes in a cascade of reactors on the characteristics of the copolymer product by computer modeling of the process. Computational experiments based on a computer model may significantly reduce the costs of conducting experiments under laboratory and, particularly, industrial conditions in real time.

EXPERIMENTAL

Previously [8, 9], we proposed an algorithm for modeling the copolymerization process performed in a continuous mode in a cascade of reactors. This algorithm is based on the Monte Carlo method according to the approach proposed by Gillespie [10, 11]. The basis of the algorithm is a cycle of the following stages implemented at certain points in times:

- calculation of reaction rates at a current ratio of particles in the reactor;
- calculation of the probabilities of their implementation based on the values of the rates and their sequential arrangement on the interval [0, 1];
- generation of a random number on the same interval, determination of the part of the interval that contains the random number, and selection of the corresponding part of the reaction interval;
- modeling the selected reaction at the level of change in the number of types of particles of the reaction

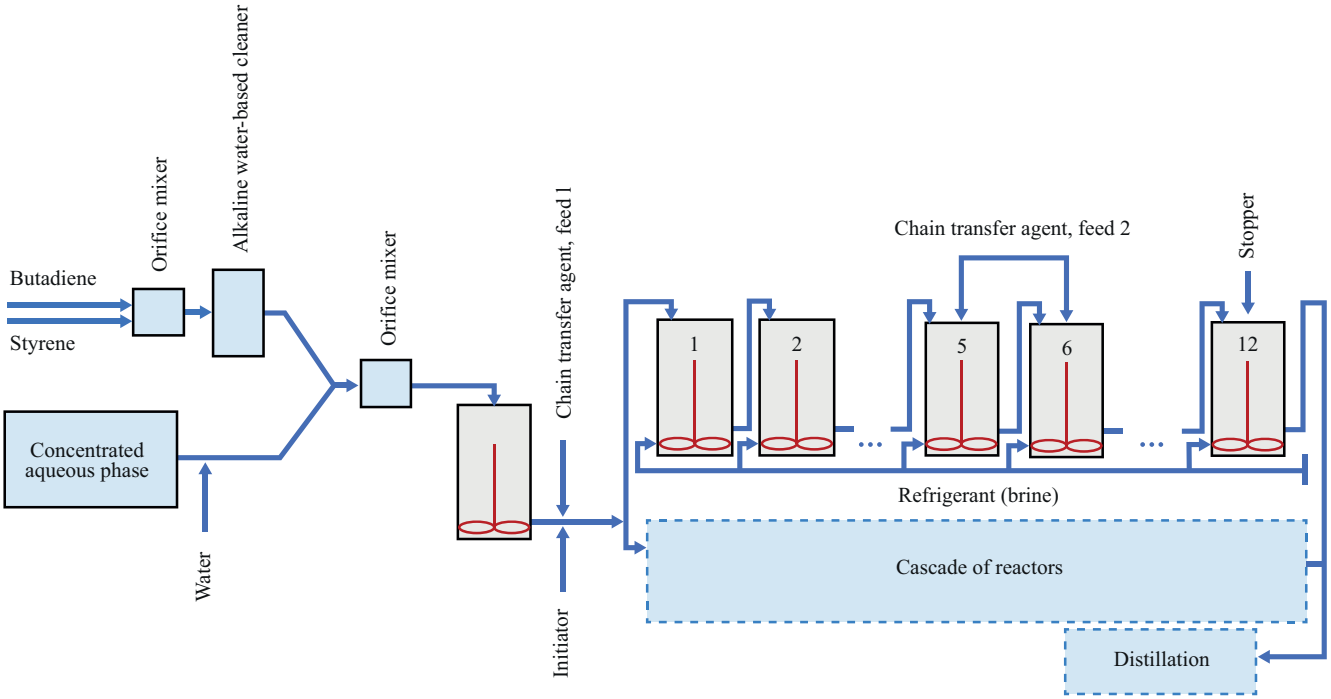


Fig. 1. Scheme of continuous production of synthetic rubber by emulsion copolymerization of butadiene with styrene

mixture (e.g., an increase in the length of growing macromolecules and a decrease in the number of monomers when modeling the growth reaction, etc.).

The condition for stopping the cycle is reaching a certain condition, e.g., achieving a predetermined value of monomer conversion.

Since the synthesis of styrene–butadiene rubber under industrial conditions is performed continuously in parallel in several cascade reactors, it should be noted that each component of the reaction mixture has its own residence time in the reactor. Within the framework of the proposed model, the residence time is a random variable characterized by the probability distribution function $p(t)$ [12].

The probability of which reactions can occur in each of the cascade reactors at a specific point in time depends directly on the types of particles of the reaction mixture (monomer, initiator, CTA, copolymer macromolecules) and the quantities in these reactors.

With the reaction selected for modeling, the time of its implementation is put in correspondence:

$$\Delta t = \frac{1}{R_{\text{sum}}} \ln\left(\frac{1}{r_p}\right),$$

wherein R_{sum} accumulates the rates of all elementary reactions that can occur and the probability of which is not zero, and r_p is a random number generated on the interval [0, 1].

The probability of an event, i.e., the presence of the particle under study in the cascade reactor under consideration during the time from t to $t + dt$, is given by the value $p(t)dt$. The function $p(t)$ depends on the type of reactor used in the process technology. In our case, the reactors in the cascade are continuous stirred-tank reactors, and $p(t)$ is represented as

$$p(t) = \left(\frac{n}{\tau}\right)^n \frac{t^{n-1}}{(n-1)!} e^{-\frac{nt}{\tau}}, \quad (1)$$

wherein τ is the average residence time of particles of the reaction mixture in one reactor, h; and n is the number of devices in the reactor cascade [13].

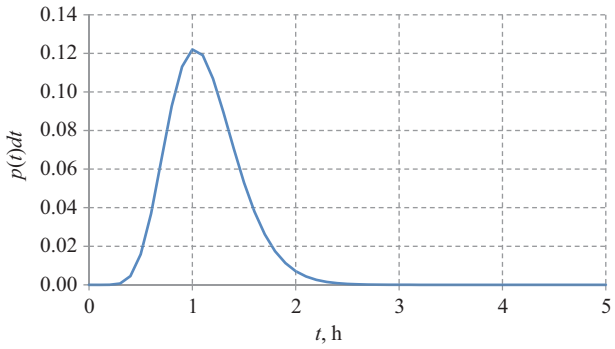


Fig. 2. Residence time distribution in a cascade of 11 reactors

Figure 2 shows the residence time distribution of the components of the reaction mixture in a cascade of 11 reactors 10.8 m^3 in volume each at a volume flow rate of C_f = 9.5982 m^3/h. At these parameters, the average residence time of particles of the reaction mixture in one reactor is 1.125 h, which corresponds to the peak of the curve in Fig. 2.

In order to model the copolymerization process in a cascade of continuous stirred-tank reactors, the residence time in the current reactor needs to be defined for each component of the mixture (molecule and macromolecule) using distribution (1). For the time interval from 0 to $t_{\max}$, a partitioning step dt is selected in such a way that the events corresponding to all residence time variants form a complete group of events. In the case considered in Fig. 2, such a time interval is the interval from 0 to 5 h with a step of 0.1 h.

In order to determine the residence time of each individual particle of the reaction mixture in the reactor under consideration, a new random value is generated from the interval [0, 1], and the value of f is selected in such a way that the following inequality is satisfied:

$$\sum_{i=1}^{f-1} p((f-1)\cdot dt) < r_p < \sum_{i=1}^{f} p(f \cdot dt).$$

This inequality characterizes the part of the interval in which the generated value is located. Accordingly, for the particle in question, the residence time in the current reactor is defined as $f \cdot dt$. Therefore, the time of transfer of particles of the reaction mixture to the next reactor after their residence time in the current reactor has expired needs additionally to be monitored.

As a result, the formation of the copolymer in the cascade of series-connected reactors is modeled. The model considers the constant flow of the initial mixture of particles of various types into the first reactor and the removal of the formed copolymer. This approach to considering molecules of the mixture and macromolecules of the product at the particle level allows us to proceed to calculate the molecular-weight and viscosity characteristics of the product.

Data on all particles involved in the process, including those formed in it, can be obtained at any time, upon reaching specific values of monomer conversion, as well as at the outlet of each reactor. Such an approach allows us to obtain the following information for each reactor:

- the number of particles of each monomer, initiator, and CTA;
- the numbers of active and inactive macromolecules of each type, the chain length, and the structure of the composition of each of them. If we additionally save data on which two or three chain links are at the end,

we can describe which types of dyads and triads of links make up the structure of macromolecules of the compound through their fractions;
- molecular-weight characteristics (number-average molecular weight M_n, weight-average molecular weight M_w, and molecular weight distribution) and viscosity characteristics (intrinsic viscosity and Mooney viscosity) of the copolymer product [14, 15].

RESULTS AND DISCUSSION

We created a program for conducting computational experiments. The approach presented was used to calculate the process of copolymerization of butadiene with styrene in several continuous stirred-tank reactors, sequentially forming a cascade (in the C# and Visual C++ environment).

By means of computational experiments, we evaluated the influence of the composition of the reaction mixture or the feed modes of various reagents on the properties of the resulting copolymer or the product produced from it. In particular, we considered the effect of the CTA feed mode on these properties by the example of conducting the process in a cascade of 11 continuous stirred-tank reactors at the following characteristics of the loaded mixture:
- mass flow rate of monomers—3.5 t/h (100 parts by weight per hour (pts. wt/h); 70 and 30 pts. wt/h for butadiene and styrene, respectively);
- initiator (pinane hydroperoxide)—0.054 pts. wt/h;
- water : monomer ratio = 220 : 100;
- working volume of reactor—10.8 m^3;
- volume flow rate—9.5982 m^3/h.

The experimental data at the given process characteristics (Table) were obtained at the Central Laboratory of *Sterlitamak Petrochemical Plant* (Sterlitamak, Bashkortostan, Russia) [8]. The molecular weight of the copolymer was controlled by an CTA as *tert*-dodecyl mercaptan, fed at several points of the reactor cascade. The CTA was continuously fed to the first reactor at a mass flow rate of 0.125 pts. wt/h and to the third and sixth reactors at a mass flow rate of 0.027 pts. wt/h.

Computational experiment 1 was carried out according to the approach we proposed, modeling 30 h of the process with the above characteristics. The results obtained were compared with the results of the production experiment (Table).

Figure 3 presents the profiles of the intrinsic viscosity of the copolymer along the reactor cascade. Figure 4 shows the dependence of the intrinsic viscosity of the copolymer on the total conversion of monomers. At the outlet of the first reactor of the cascade, the discrepancy between the result of the computational experiment and the production data was maximum (30%) At the outlet of the last reactor of the cascade, the discrepancy was 3.6%, which demonstrated the agreement between the computational and production data.

Table. Results of production experiment

Reactor number	Mooney viscosity	Intrinsic viscosity, dL/g	Monomer conversion, %
1	–	0.73	5.5
2	–	–	14.1
3	–	0.86	23.7
4	–	1.28	29.6
5	–	1.28	32.0
6	–	–	41.8
7	38	1.66	51.3
8	–	1.70	55.8
9	79	2.24	64.0
10	–	2.31	69.0
11	87	2.42	70.4

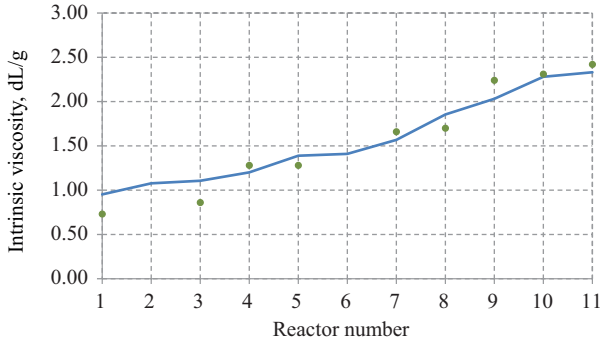


Fig. 3. Dependencies of the calculated (line) and experimental (points) values of intrinsic viscosity along the reactor cascade

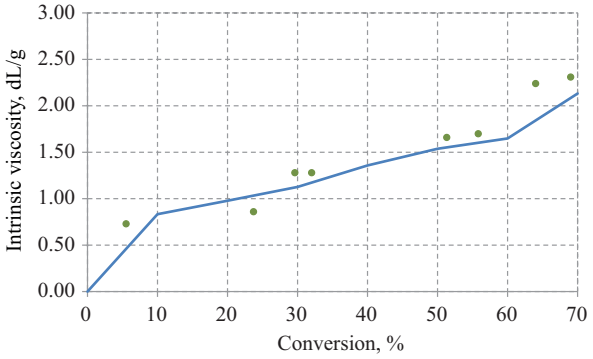


Fig. 4. Dependencies of the calculated (line) and experimental (points) values of intrinsic viscosity on conversion of monomers

The behavior of the intrinsic viscosity curve of the resulting copolymer is controlled by the change in the amount of the CTA in the cascade reactors (Fig. 5). More than half of the loaded portion of the CTA is consumed in the first and second reactors. This significantly slows down the increase in the intrinsic viscosity therein when compared with the reactors of the second half of the cascade.

The CTA is additionally fed for the second time to the third reactor, and for the third time to the sixth reactor of the cascade. As a result, it can be observed that the intrinsic viscosity of the product changes slowly: from 1.10 dL/g in the third reactor to 1.41 dL/g in the sixth reactor. However, due to the active consumption of CTA particles and, accordingly, the smaller amount in the last reactors of the cascade, an active increase in the molecular weight and intrinsic viscosity of the copolymer can be observed.

A similar change can also be observed in the curve demonstrating an increase in the copolymer polydispersity (the ratio of the weight-average molecular weight to the number-average molecular weight) with an increase in the reactor number (Fig. 6). The polydispersity in the cascade reactors changes in the range from 2 to 4.3, which complies with standards for styrene–butadiene rubber synthesized by low-temperature free-radical copolymerization [3].

The molecular weight distribution describes the proportions of macromolecules with different molecular weights in the copolymer. To construct this distribution using data on all chains of the formed copolymer obtained in the computational experiment, by analogy with gel chromatography, the “dead” macromolecules of the copolymer that have left the last reactor of the cascade need to be fractionated. For this purpose, we form groups (fractions) in which the molecular weights of macromolecules differ by ΔM. Then, for each group formed, we calculated the ratio of the sum of the molecular weights of macromolecules in the group to the sum of the molecular weights of macromolecules in all groups is, i.e., the weight fraction of the group, which must be normalized by dividing the obtained value by ΔM [8]. In the case under consideration, the curve presenting the change in the normalized weight fraction with an increase in the group weight is shown in Fig. 7 at two time points: after 15 and 30 h of process modeling.

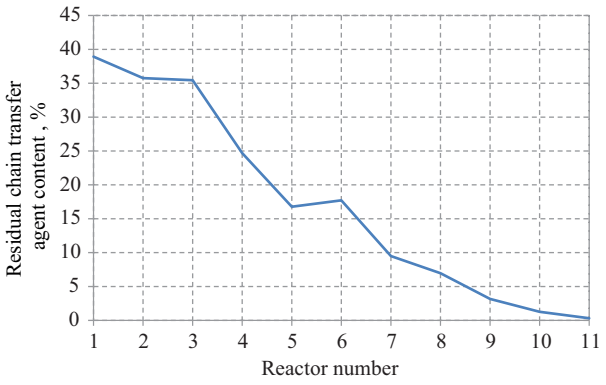


Fig. 5. Dependence of the calculated residual CTA content along the reactor cascade

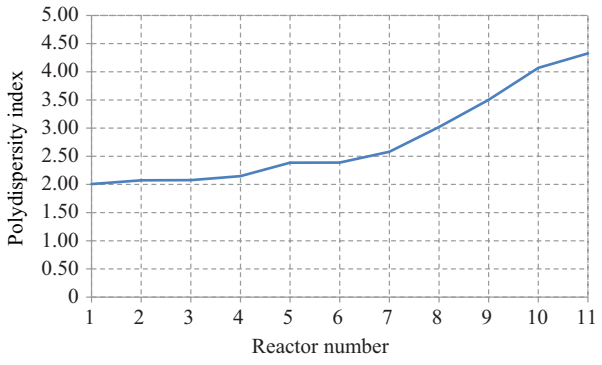


Fig. 6. Calculated polydispersity dependence along the reactor cascade

Fig. 7. Differential molecular weight distribution curve of the copolymer after 15 h (dotted line) and 30 h (solid line) of process modeling

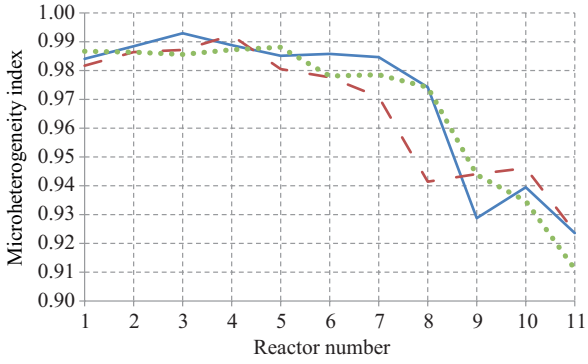


Fig. 9. Dependencies of the microheterogeneity index of the copolymer along the reactor cascade

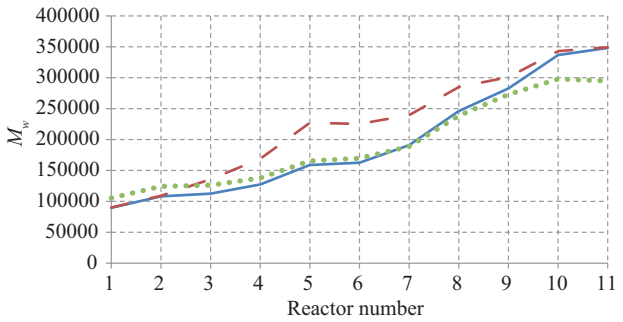


Fig. 8. Dependencies of the weight-average molecular weight along the reactor cascade

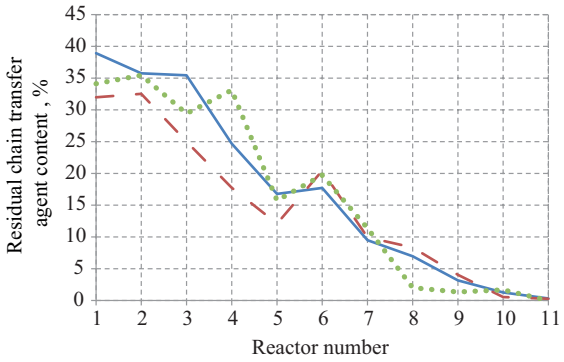


Fig. 10. Calculated residual CTA content dependencies along the reactor cascade

The proposed approach to modeling and the program developed on its basis permits the microstructure of the copolymer changes to be studied when changing the technological scheme of the copolymerization process under industrial conditions or when varying the process characteristics. Thus, the sequences in which butadiene and styrene units are linking together in macromolecules can be studied. Further in the work, we considered additional modes of continuous feed of the CTA and their effect on the product properties, while maintaining its total amount at the same level:

- to two points with a larger amount of the CTA in the second half of the reactor cascade: the first point (reactor 1), 0.125 pts. wt/h; and the second point (reactor 6), 0.054 pts. wt/h (computational experiment 2);
- at three points with a different CTA distribution: the first point (reactor 1), 0.109 pts. wt/h; the second point (reactor 3), 0.035 pts. wt/h; and the third point (reactor 6), 0.035 pts. wt/h (computational experiment 3).

In the figures below, the solid lines show the dependencies for the three-point mode of feeding the CTA in the production experiment (computational experiment 1); the dashed lines, the two-point mode of feeding the CTA (computational experiment 2); and the dotted lines, the three-point mode of feeding the CTA with a different distribution of the CTA (computational experiment 3).

Figures 8 and 9 demonstrate the profiles of the weight-average molecular weight of the copolymer and the microheterogeneity index along the reactor cascade in the above modes of feeding the CTA. Figure 10 presents the dependence of the residual CTA content along the reactor cascade for each of the modes.

Figures 11–13 show the dependencies of the fractions of various types of dyads in copolymer macromolecules along the reactor cascade in the modes of feeding the CTA to the first, third, and sixth reactors of the cascade in accordance with the experimental design at the production facility.

Thus, changing the mode of feeding the CTA to the reactor cascade (choosing the feed points) affects the characteristics of the formed copolymer. The three-point feed of the CTA helps to reduce the weight-average molecular weight of the formed product, narrow the spread of microheterogeneity index, and a corresponding decrease in the tendency to form long blocks in the copolymer.

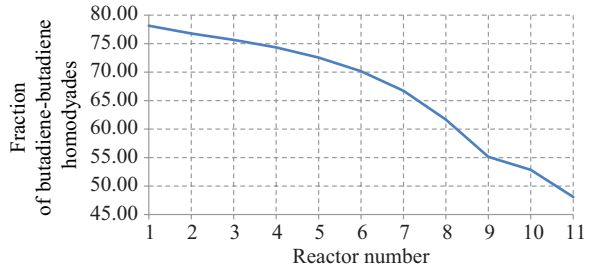


Fig. 11. Dependence of the fraction of butadiene–butadiene homodyads in copolymer chains along the reactor cascade

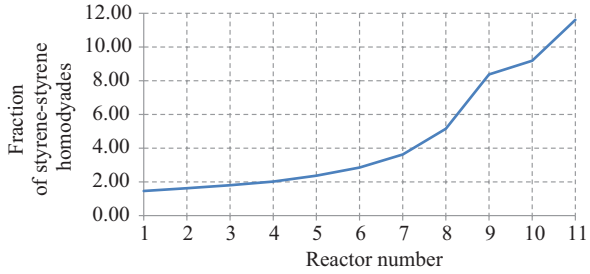


Fig. 12. Dependence of the fraction of styrene–styrene homodyads in copolymer chains along the reactor cascade

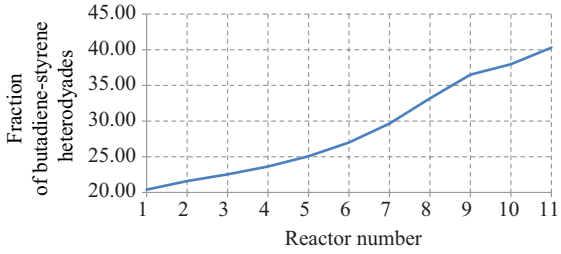


Fig. 13. Dependence of the fraction of butadiene–styrene heterodyads in copolymer chains along the reactor cascade

CONCLUSIONS

Thus, the proposed approach based on modeling the formation of butadiene–styrene copolymer macromolecules using the Monte Carlo method adequately describes its production in a cascade of continuous stirred-tank reactors. Thanks to the information obtained by the modeling, the molecular-weight and viscosity properties of the formed copolymer in dynamics at a constant feed flow rate under various production conditions can be studied. This allows the influence of the production mode to be assessed. Based on the results of the computational experiments, it was noted that, with an increase in the process time, the fraction of high-molecular-weight fractions of the copolymer increases. This occurs due to an increase in the content of styrene homodyads in the forming copolymer chains. This, in turn, renders the product produced from it less elastic. Fractional feeding of the CTA to three reactors helps to reduce the molecular weight of the final product, narrow the spread of microheterogeneity index, and, as a result, decreases the probability of the formation of long blocks in the copolymer.

Acknowledgments

The research was supported by the Russian Science Foundation grant No. 24-21-00186, https://rscf.ru/project/24-21-00186/.

Authors' contribution

All authors equally contributed to the research work.

The authors declare no conflict of interest.

REFERENCES

1. Arzhakov M.S., *et al*. *Vysokomolekulyarnye soedineniya* (*Molecular Compounds*). Moscow: Yurait; 2024. 340 p. (in Russ.). ISBN 978-5-534-01322-1
2. Carpio R.R., Feital T., Câmara M.M., *et al*. Digital Twin for the SBR Cold Emulsion Copolymerization Process. *Macromol. React. Eng*. 2024;18(3):2300055. https://doi.org/10.1002/mren.202300055
3. Kirpichnikov P.A., Beresnev V.V., Popova L.M. *Al'bom tekhnologicheskikh skhem osnovnykh proizvodstv promyshlennosti sinteticheskogo kauchuka* (*Album of Technological Schemes of the Main Productions of the Synthetic Rubber Industry*). Moscow: Al'yans; 2017. 224 p. (in Russ.).
4. Maevskii V.A. Stabilization of polymer quality indicators in a chemical reactor. *Izvestiya Sankt-Peterburgskogo gosudarstvennogo tekhnologicheskogo instituta* (*tekhnicheskogo universiteta*) = *Bulletin of the Saint Petersburg State Institute of Technology* (*Technical University*). 2022;60(86):75–82 (in Russ.). https://doi.org/10.36807/1998-9849-2022-60-86-75-82

СПИСОК ЛИТЕРАТУРЫ

1. Аржаков М.С. и др. *Высокомолекулярные соединения*; под ред. А.Б. Зезина. М.: Юрайт; 2024. 340 с. ISBN 978-5-534-01322-1
2. Carpio R.R., Feital T., Câmara M.M., *et al*. Digital Twin for the SBR Cold Emulsion Copolymerization Process. *Macromol. React. Eng*. 2024;18(3):2300055. https://doi.org/10.1002/mren.202300055
3. Кирпичников П.А., Береснев В.В., Попова Л.М. *Альбом технологических схем основных производств промышленности синтетического каучука*. М.: АльянС; 2017. 224 с.
4. Маевский В.К. Стабилизация показателей качества полимера в химическом реакторе. *Известия СПбГТИ* (*ТУ*). 2022;60(86):75–82. https://doi.org/10.36807/1998-9849-2022-60-86-75-82
5. Кафаров В.В., Дорохов И.Н. *Системный анализ процессов химической технологии: основы стратегии*. М.: Юрайт; 2018. 499 с. ISBN 978-5-534-06991-4

5. Kafarov V.V., Dorokhov I.N. *Sistemnyi analiz protsessov khimicheskoi tekhnologii: osnovy strategii* (*System Analysis of Chemical Technology Processes: Fundamentals of Strategy*). Moscow: Yurait; 2018. 499 p. (in Russ.). ISBN 978-5-534-06991-4
6. Gartner Ш T.E., Jayaraman A. Modeling and simulations of polymers: A Roadmap. *Marcomolecules*. 2019;52(3): 755–786. https://doi.org/10.1021/acs.macromol.8b01836
7. Averko-Antonovich I.Yu., Bikmullin R.T. *Metody issledovaniya svoistv polimerov* (*Methods for Studying the Properties of Polymers*). Textbook. Kazan: KSTU; 2002. 603 p. (in Russ.). ISBN 5-7882-0221-3
8. Mikhailova T.A., Miftakhov E.N., Mustafina S.A. *Issledovanie protsessov promyshlennogo sinteza polimerov metodami matematicheskogo modelirovaniya s primeneniem tekhnologii oblachnykh vychislenii* (*Study of the Processes of Industrial Synthesis of Polymers by Mathematical Modeling Methods with Cloud Computing Technologies*). Monograph. Ufa: Editorial and Publishing Center of UUST; 2023. 164 p. (in Russ.).
9. Mikhailova T.A., Miftakhov E.N., Nasyrov I.Sh., Mustafina S.A. Modeling of continuous free-radical butadiene-styrene copolymerization process by the Monte Carlo method. *Vestnik Voronezhskogo gosudarstvennogo universiteta inzhenernykh tekhnologii = Proceedings of the Voronezh State University of Engineering Technologies*. 2016;2(68):210–217 (in Russ.). https://doi.org/10.20914/2310-1202-2016-2-210-217
10. Gillespie D. Exact Stochastic Simulation of Coupled Chemical Reactions. *J. Phys. Chem*. 1977;81(25):2340–2361. https://doi.org/10.1021/j100540a008
11. Trigilio A.D., Marien Y.W., Van Steenberge P.H.M., *et al*. Gillespie-Driven kinetic Monte Carlo Algorithms to Model Events for Bulk or Solution (Bio)Chemical Systems Containing Elemental and Distributed Species. *Ind. Eng. Chem. Res*. 2020;59(41): 18357–18386. https://doi.org/10.1021/acs.iecr.0c03888
12. Aris R. *Analiz protsessov v khimicheskikh reaktorakh* (*Analysis of Processes in Chemical Reactors*): transl. from Engl. Leningrad: Khimiya; 1989. 327 p. (in Russ.).
[Aris R. *Introduction to the Analysis of Chemical Reactors*. NJ: Prentice Hall; 1965. 337 p.]
13. Rawlings J.B., Ekerdt J.G. *Chemical Reactor Analysis and Design Fundamentals*. Madison: Nob Hill Publishing; 2002. 610 p.
14. Mikhailova T., Mustafina S., Mikhailov V. Automation of data processing of the results of the chemical experiment on modeling the production of synthetic rubber using Microsoft Excel. *J. Phys.: Conf. Ser*. 2021;2092(1):012003. https://doi.org/10.1088/1742-6596/2092/1/012003
15. Miftakhov E., Mustafina S., Mikhailova T., *et al*. Application of cloud computing technologies for the study of physical and chemical processes. In: *The 2022 8th International Conference on Information Technology and Nanotechnology* (*ITNT*). IEEE; 2022. 4 p. https://doi.org/10.1109/ITNT55410.2022.9848608

6. Gartner III T.E., Jayaraman A. Modeling and simulations of polymers: A Roadmap. *Marcomolecules*. 2019;52(3): 755–786. https://doi.org/10.1021/acs.macromol.8b01836
7. Аверко-Антонович И.Ю., Бикмуллин Р.Т. *Методы исследования свойств полимеров:* учебное пособие. Казань: КГТУ; 2002. 603 с. ISBN 5-7882-0221-3
8. Михайлова Т.А., Мифтахов Э.Н., Мустафина С.А. *Исследование процессов промышленного синтеза полимеров методами математического моделирования с применением технологий облачных вычислений:* монография. Уфа: Уфимский университет науки и технологий, РИЦ; 2023. 164 с.
9. Михайлова Т.А., Мифтахов Э.Н., Насыров И.Ш., Мустафина С.А. Моделирование непрерывного процесса свободно-радикальной сополимеризации бутадиена со стиролом методом Монте-Карло. *Вестник Воронежского государственного университета инженерных технологий*. 2016;2(68):210–217. https://doi.org/10.20914/2310-1202-2016-2-210-217
10. Gillespie D. Exact Stochastic Simulation of Coupled Chemical Reactions. *J. Phys. Chem*. 1977;81(25):2340–2361. https://doi.org/10.1021/j100540a008
11. Trigilio A.D., Marien Y.W., Van Steenberge P.H.M., *et al*. Gillespie-Driven kinetic Monte Carlo Algorithms to Model Events for Bulk or Solution (Bio)Chemical Systems Containing Elemental and Distributed Species. *Ind. Eng. Chem. Res*. 2020;59(41):18357–18386. https://doi.org/10.1021/acs.iecr.0c03888
12. Арис Р. *Анализ процессов в химических реакторах*: пер. с англ. Л.: Химия; 1989. 327 с.
13. Rawlings J.B., Ekerdt J.G. *Chemical Reactor Analysis and Design Fundamentals*. Madison: Nob Hill Publishing; 2002. 610 p.
14. Mikhailova T., Mustafina S., Mikhailov V. Automation of data processing of the results of the chemical experiment on modeling the production of synthetic rubber using Microsoft Excel. *J. Phys.: Conf. Ser*. 2021;2092(1):012003. https://doi.org/10.1088/1742-6596/2092/1/012003
15. Miftakhov E., Mustafina S., Mikhailova T., *et al*. Application of cloud computing technologies for the study of physical and chemical processes. In: *The 2022 8th International Conference on Information Technology and Nanotechnology* (*ITNT*). IEEE; 2022. 4 p. https://doi.org/10.1109/ITNT55410.2022.9848608

About the authors

Tatiana A. Mikhailova, Cand. Sci. (Phys.-Math.), Docent, Associate Professor, Department of Mathematical and Computer Modeling, Ufa University of Science and Technology (UUST) (32, Zaki Validi ul., Ufa, 450076, Russia). E-mail: t.a.mihailova@yandex.ru. Scopus Author ID 56177484100, ResearcherID Q-7593-2017, RSCI SPIN-code 3569-2170, https://orcid.org/0000-0002-9096-4385

Svetlana A. Mustafina, Dr. Sci. (Phys.-Math.), Professor, Vice-Rector for Digital Transformation, Head of the Department of Mathematical and Computer Modeling, Ufa University of Science and Technology (UUST) (32, Zaki Validi ul., Ufa, 450076, Russia). E-mail: mustafina_sa@mail.ru. Scopus Author ID 6603592002, Researcher ID O-6833-2015, RSCI SPIN-code 1120-5035, https://orcid.org/0000-0002-6363-1665

Об авторах

Михайлова Татьяна Анатольевна, к.ф.-м.н., доцент, доцент кафедры математического и компьютерного моделирования, ФГБОУ ВО «Уфимский университет науки и технологий» (УУНиТ) (450076, Россия, г. Уфа, ул. Заки Валиди, д. 32). E-mail: t.a.mihailova@yandex.ru. Scopus Author ID 56177484100, ResearcherID Q-7593-2017, SPIN-код РИНЦ 3569-2170, https://orcid.org/0000-0002-9096-4385

Мустафина Светлана Анатольевна, д.ф.-м.н., профессор, проректор по цифровой трансформации, заведующий кафедрой математического и компьютерного моделирования, ФГБОУ ВО «Уфимский университет науки и технологий» (УУНиТ) (450076, Россия, г. Уфа, ул. Заки Валиди, д. 32). E-mail: mustafina_sa@mail.ru. Scopus Author ID 6603592002, ResearcherID O-6833-2015, SPIN-код РИНЦ 1120-5035, https://orcid.org/0000-0002-6363-1665

Translated from Russian into English by V. Glyanchenko
Edited for English language and spelling by Dr. David Mossop