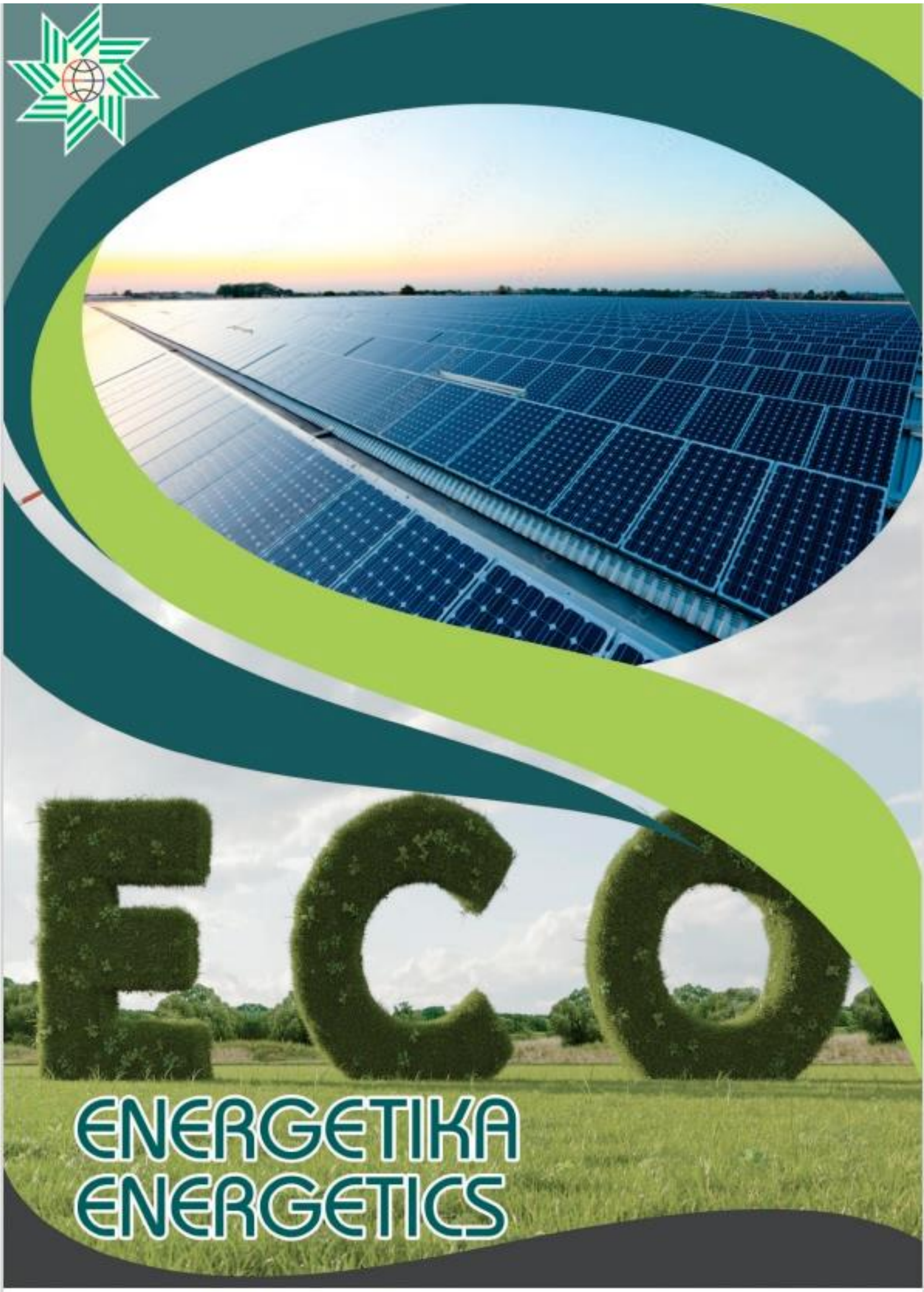

ECO
ENERGETIKA
ENERGETICS

Published from 2004
Ministry of Press and Information
of Azerbaijan Republic,
Registration number 3337, 07.03.2011

ISSN 1816-2126
Number 03, 2024
Section: English

ECOENERGETİCS

PUBLISHING OFFICE
5, M.Rahim, AZ-1073, Baku Azerbaijan
Tel.: 99412 538-23-70,
99412 538-40-25
Fax: 99412 538-51-22

E-mail: info@ieeacademy.org
ekoenergetics@gmail.com
Internet: http://ieeacademy.org
www.innovationresearch.az

Contents

Graphene-Enhanced Poly(Ester Amide)s for Sustainable Applications

E.A.Khanmamadova, R.G.Abaszade

Azerbaijan State Oil and Industry University
khanman.ea@gmail.com , abaszada@gmail.com

Abstract: This work reports the synthesis of poly(ester amide)s from renewable resources, focusing on their thermal, mechanical, and environmental properties, besides some potential applications in sustainable polymer development and renewable fuel innovations. Synthesis was done by regioselective polymerization with diol-diamide monomers and the diacid diacyl chloride (Z)-octadec-9-enedioyl dichloride (D18:1). The resulting materials have superior thermal stability, improved crystallinity, and controlled dispersity, which enables their use in advanced engineering applications. Besides, propanol, n-butanol, and 1-pentanol are higher-order alcohol additives, and their effects on fuel properties, engine performance, and emission parameters were studied when blended with diesel-biodiesel. These blends have the potential for cold flow improvement and NOx emission reduction. It also introduces graphene-based nanomaterials into the polymer matrix, hence enhancing its mechanical, electrical, and thermal properties for advanced engineering and energy applications.

Keywords: Poly(ester amide)s, renewable resources, polymerization, (Z)-octadec-9-enedioyl dichloride, hydrogen bonding, thermal stability, crystallinity, diesel-biodiesel blends, engine performance, NOx emissions, graphene nanomaterials, mechanical properties, energy applications.

1.INTRODUCTİON

This work bridges the work in sustainable polymer synthesis and renewable energy development, targeting twin improvements in material science as well as energy efficiency. [1-7] The resulting PEAs, synthesized with bio-based monomers like succinic acid and D18:1, present excellent thermal stability and crystallinity, answering current demands related to high-performance, sustainable polymers. Simultaneously, the higher alcohol additives in diesel-biodiesel blends aim at optimization of fuel properties and a reduction of harmful emissions. Further integration of graphene-based nanomaterials into a polymer matrix enhances such material properties. Hence, these are indeed crucial developments for applications in engineering and renewable energies.[8]

The synthesis process starts by preparing the (Z)-octadec-9-enedioyl dichloride (D18:1) in a two-neck round-bottom flask fitted with a reflux condenser. The reaction conditions include a slow addition of oxalyl chloride, cooling of the sample, and finally purification of the product. [9-15] This reaction produces diacid chloride with high purity ready for subsequent polymerization. In a similar way, the diol-diamide monomers like N,N'-bis(2-hydroxyethyl)butanediamide (HEBDA) are prepared by the reaction between succinic acid and ethanolamine under controlled conditions that yield the desired product.[16-19]

The polymerization of D18:1 with 2,2′-bis(2-oxazoline) and other monomers was conducted in a nitrogen atmosphere at temperatures from 140 °C to 190 °C, depending on the reaction conditions. Such PEA materials exhibit excellent mechanical properties, including high melting points and narrow temperature differences between crystallization and melting-a very important characteristic for thermal stability in engineering applications.[20-21]

2. EXPERİMENTAL DETAİL

Synthesis of Diacid Chloride (D18:1)

To prepare D18:1, 7.02 g of D18:1 (22.47 mmol) and 105 mL of CH_2Cl_2 were added to a 250 mL round-bottom flask with a reflux condenser. After complete dissolution, the solution was cooled to 0 °C. Then, 5.76 mL (67.16 mmol, 3 equivalents) of oxalyl chloride was added slowly under stirring.

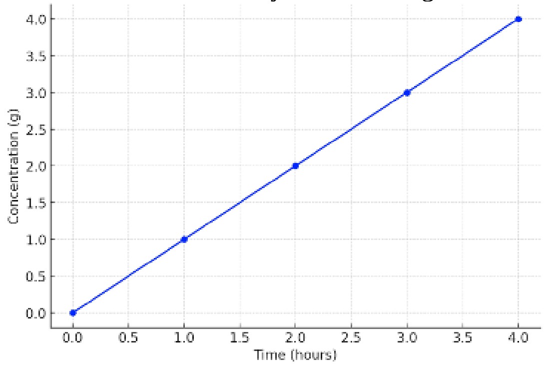


Fig 1. Synthesis of D18:1(Diacid Chloride)

The reaction proceeded for 4 hours at room temperature, with HCl vapors trapped in a NaOH solution. (Figure 1) The solvent and excess reagents were removed, yielding 7.81 g of high-purity diacid chloride.[22-28]

Synthesis of Diol Diamide Monomers (HEBDA)

The diol diamide monomer HEBDA was synthesized by reacting 9.784 g of succinic acid (82.9 mmol) with 100 mL of ethanolamine (1.657 mol, 20 equivalents). [29, 32,40] The mixture was heated at 160°C with stirring for 5 hours, resulting in a clear solution. After cooling, the product was precipitated in chloroform, filtered, and dried. (Figure 2) The white crystalline product showed excellent purity and thermal stability, with a T5% of 205°C and a melting point of 144°C.

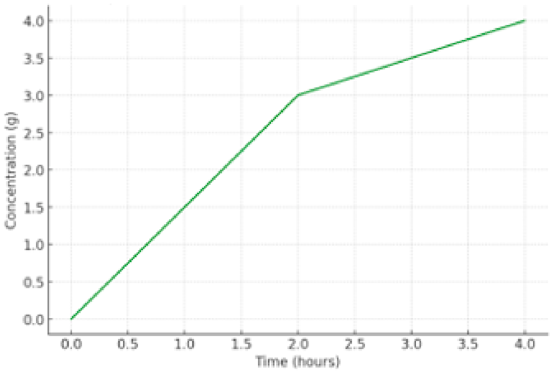


Fig.2. Synthesis of HEBDA (Diol diamide monomer)

Polymerization of D18:1 and HED18:1DA

The polycondensation of D18:1 with HED18:1DA was carried out in a two-neck Schlenk reactor under a nitrogen atmosphere. [30,31,38] The system was heated to 160 °C, where the mixture turned into a clear liquid. $Ti(OBu)_4$ was used as a catalyst, and the reaction was continued at 170 °C for 4 hours. The final product was purified and dried, resulting in a polymer yield of 82%. (Figure 3) The polymer showed an M_n value of 12,000 g/mol and a dispersity (Đ) of 1.97, indicating minimal side reactions during the synthesis. Thermal analysis revealed a T5% of 299°C, confirming the polymer's excellent thermal stability.

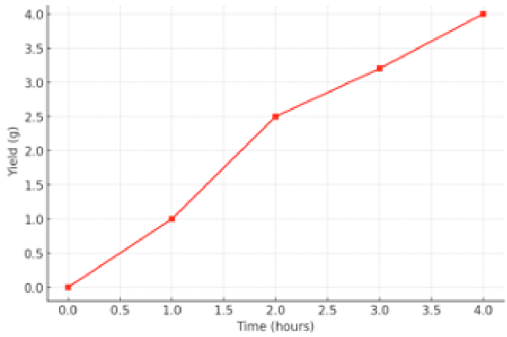


Fig.3. Polymerization progress (Polymer yield)

The thermal stabilities of D18:1, HEBDA, and the final polymer have been compared based on their T5% (temperature at 5% weight loss) and melting points as follows:

D18:1 (Diacid Chloride): T5%=200°C, Melting Point=150°C

HEBDA (Diol Diamide Monomer): T5% = 220°C, MP = 144°C

Final Polymer (D18:1 + HED18:1DA): T5% = 299°C, Melting Point = 299°C. (Figure 4)

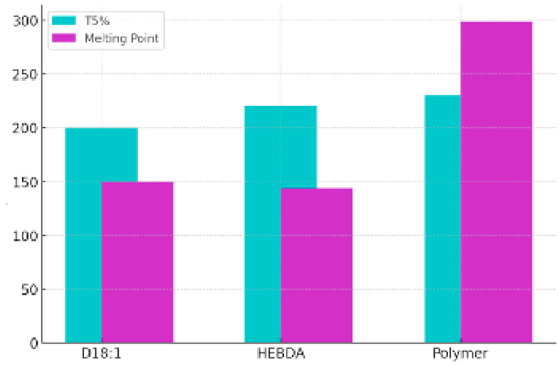


Fig.4. Thermal Stability Comparison of D18:1, HEBDA, and the Final Polymer: T5% and Melting Point

The polymer has much improved thermal stability, with T5% and mp at 299°C, showing better heat resistances compared to the monomers.

RESULTS

With PEAs synthesized from renewable sources-pecifically D18:1 and HEBDA-a great improvement in polymer design with control on regioselectivity becomes relevant. This class of polymers exhibits higher thermal stability due to intra-hydrogen bonding on the amide groups compared with polyesters containing aliphatic residues exclusively. High crystallinity of the resulting polymers could be observed, along with good control over dispersity that is very important for certain applications requiring predictable material performance.

Nanomaterials from graphene that are included in the polymer matrix were further subjected to outstanding mechanical properties along with electrical and thermal. Such an integrated graphene-based multifunctional nanomaterial would thus optimize the general performance of such PEAs toward high engineering applications and energy-related purposes.[44-47].

Besides that, the addition of higher alcohols into diesel-biodiesel mixtures improved the fuel cold flow characteristics, therefore important to the performance at low-temperature conditions. [33-38] For instance, propanol, n-butanol, and 1-pentanol were evaluated in mixtures; improved cold filter plugging points and pour points were recorded compared to standard diesel-biodiesel mixtures. Moreover, the mixtures containing higher alcohols showed lower NOx emissions, therefore significant in reducing the environmental impact of internal combustion engines.[43]

3. CONCLUSION

This work will discuss the synthesis of renewable resource-based advanced poly(ester amide)s and their graphene-based nanomaterials with improved thermal, mechanical, and environmental properties. These materials have great potential in advanced engineering applications, particularly for those industries requiring high-performance polymers. Furthermore, optimization of diesel-biodiesel mixes with higher alcohols is seen to realize promises in fuel improvements, especially in fuel property improvements and emission reductions. They thus play a major role toward energy sustainability. Results, combining material science and energy sustainability, are fundamental for responding properly to the big demands facing our environment and technologies in pressing issues.

REFERENCES

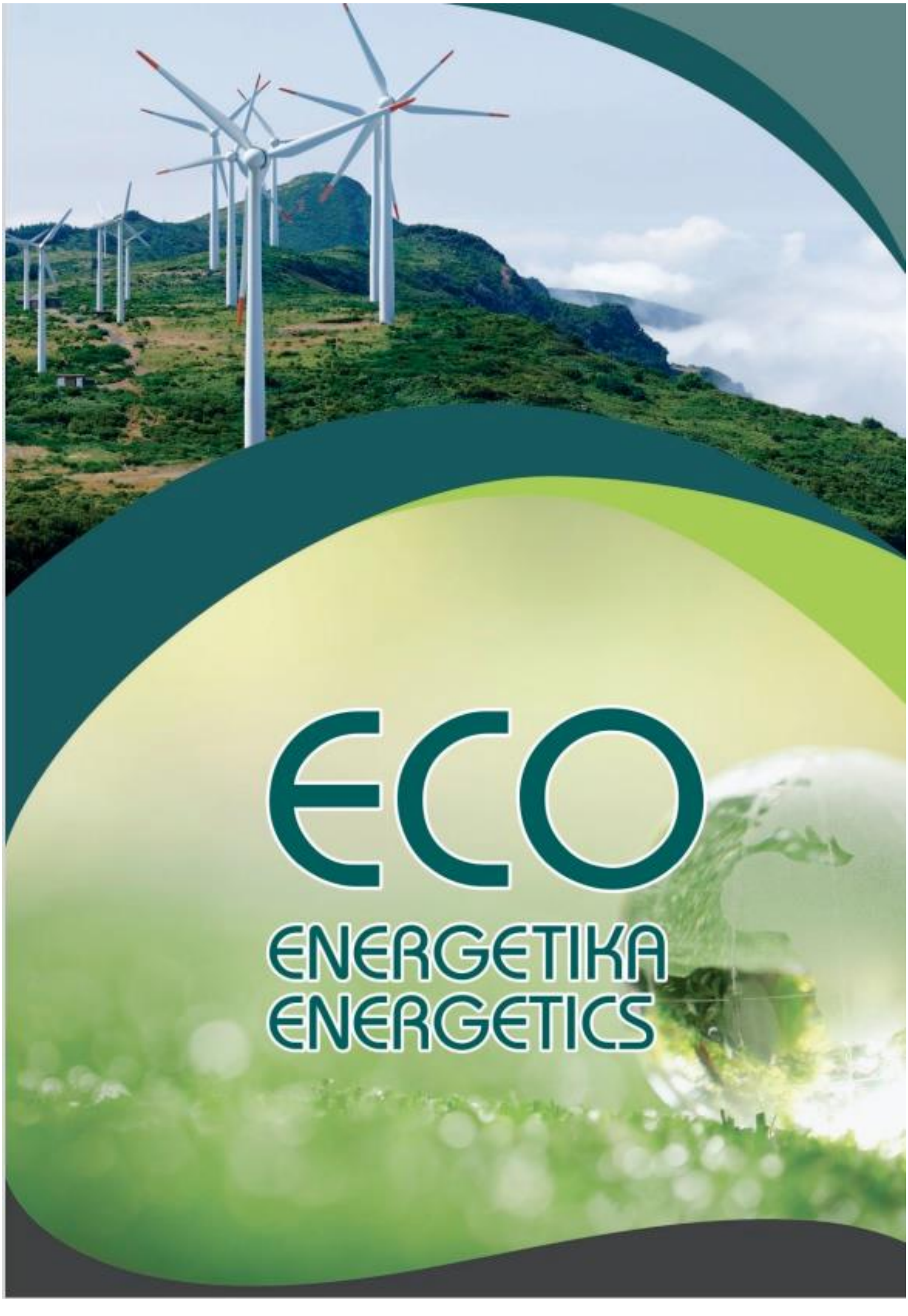
1. N.N. Thi Hang, B. Frédéric, B. Andreas, B. Véronique, G. Philippe, Synthesis of new biobased linear poly(ester amide)s, European Polymer Journal 121, 109314, 2019.
2. M. Rebecca, V. Keith, C. Greg, J. Shan, Biobased foams for thermal insulation: material selection, processing, modelling, and performance, RSC Adv., 11, 4375–4394, 2021.
3. B. Goran, Bioenergy and water—the implications of large-scale bioenergy production for water use and supply, Global Environmental Change 12, 253–271, 2002.
4. B. Sharma, A. Singh, A. Sharma, A. Dubey, V. Gupta, R.G. Abaszade A.K. Sundramoorthy, N. Sharma, S. Arya, Synthesis and characterization of zinc selenide/graphene oxide (ZnSe/GO) nanocomposites for electrochemical detection of cadmium ions, Applied Physics A 130:297, 2024; https://doi.org/10.1007/s00339-024-07472-0
5. E.A. Khanmamedova The ımpact of radıoactıve radıatıon on the electrıcal transmıssıon propertıes of graphene oxıde (GO), cambridge, uk: v ınternational scientific and practical conference «educatıon and scıence of today: Intersectoral ıssues and development of scıences» August 18, pp.159-163, 2023.
6. N.A. Guliyev, R.G. Abaszade, E.A. Khanmammadova, E.M. Azizov, Synthesis and analysis of nanostructured graphene oxide, Journal of Optoelectronic and Biomedical Materials, 15(1), 23–30 2023.
7. R.G. Abaszade, O.A. Kapush, A.M. Nabiyev, Properties of carbon nanotubes doped with gadolinium, Journal of Optoelectronic and Biomedical Materials, 12(3), 61–65. 2020.
8. A.G. Mammadov, R.G. Abaszade, V.O. Kotsyubynsky, E.Y. Gur, I.Y. Bayramov, E.A. Khanmamadova, O.A. Kapush, Photoconductivity of carbon nanotubes, Technical and Physical Problems of Engineering, 14(3), 155-160 (2022).
9. R.G. Abaszade, E.M. Aliyev, A.G. Mammadov, E.A. Khanmamadova, A.A. Guliyev, F.G. Aliyev, R.I. Zapukhlyak, H.F. Budak, A.E. Kasapoglu, T.O. Margitych, A. Singh, S. Arya, E. Gür, M.O. Stetsenko, Investigation of thermal properties of gadolinium doped carbon nanotubes, Physics and Chemistry of Solid State, 25(1), 142-147 (2024); https://doi.org/10.15330/pcss.25.1.142-147
10. R.G. Abaszade, A.G. Mammadov, E.A. Khanmamedova, F.G. Aliyev, V.O. Kotsyubynsky, E. Gür, B.D. Soltabayev, T.O. Margitych, M.O. Stetsenko, A. Singh, S. Arya, Photoconductivity of functionalized carbon nanotubes, Digest Journal of Nanomaterials and Biostructures, 19(2), pp.837-843, 2024.
11. V.M. Boychuk, R.I. Zapukhlyak, R.G. Abaszade, V.O. Kotsyubynsky, M.A. Hodlevsky, B.I. Rachiy, L.V. Turovska, A.M. Dmytriv, S.V. Fdorchenko, Solution combustion synthesized NiFe2O4/reduced graphene oxide composite nanomaterials: morphology and electrical conductivity, Physics and Chemistry of Solid State vol.23, № 2, pp.815-824, 2022.
12. R.G. Abaszade, Synthesis and analysis of flakes graphene oxide, Journal of Optoelectronic and Biomedical Materials, 14(3), 107–114 (2022); https://doi.org/10.15251/JOBM.2022.143.107
13. R.G. Abaszade, A.G. Mammadova, E.A. Khanmammadova, İ.Y. Bayramov, R.A. Namazov Kh.M. Popal, S.Z. Melikova, R.C. Qasımov, M.A. Bayramov, N.İ. Babayeva, Electron paramagnetic resonance study of gadoliniumum doped graphene oxide, Journal of Ovonic Research, Vol.19(2), pp.259-263, 2023.
14. R.G. Abaszade, A.G. Mammadov, I.Y. Bayramov, E.A. Khanmamadova, V.O. Kotsyubynsky, O.A. Kapush, V.M. Boychuk, E.Y. Gur, Structural and electrical properties of sulfur-doped graphene oxide/graphite oxide composite, Physics and Chemistry of Solid State vol.25, № 2, pp.256-260, 2022.
15. R.G. Abaszade, A.G. Mammadov, I.Y. Bayramov, E.A. Khanmamadova, V.O. Kotsyubynsky, E.Y. Gur, O.A. Kapush,

Modeling of voltage-ampere characteristic structures on the basis of graphene oxide/sulfur compounds, Technical and Physical Problems of Engineering, 14(2), 302-306, 2022.

16. N. Ivanichok, P. Kolkovskyi, O. Ivanichok, V. Kotsyubynsky, V. Boychuk, B. Rachiy, M. Bembenek, Ł. Warguła, R. Abaszade, L. Ropyak, Effect of Thermal Activation on the Structure and Electrochemical Properties of Carbon Material Obtained from Walnut Shells, Materials, 17(2514), 1-21, 2024; https://doi.org/10.3390/ma17112514
17. R.Moradi, N.Pour Khalili, E.Khanmamadova, R.Abaszade, Functionalized Carbon Nanostructures for Flexible Electronics. In: Barhoum, A., Deshmukh, K. (eds) Handbook of Functionalized Carbon Nanostructures. Springer, Cham. pp.2581-2614, 2024; https://doi.org/10.1007/978-3-031-14955-9_71-1
18. M.O. Stetsenko, R.G. Abaszade, X-ray phase analysis of carbon nanotubes obtained by the arc discharge method, UNEC J. Eng. Appl. Sci. 3(1) pp.15-20, 2023; https://doi.org/10.61640/ujeas.2023.0503
19. Sh. Zhang, X. Sun, L. Wu, B. Ai, Haoran Sun and Yufeng Chen, Thermal control materials of carbon/SiO2 composites with a honeycomb structure, RSC Adv., 14, 34081, 2024.
20. E.A. Khanmamedova, Electrical conductivity properties of graphene oxide, NO. 32(151) (2023): 7th Ispc «Current Issues And Prospects For The Development Of Scientific Research» (April 19-20, 2023; Orléans, France). https://archive.interconf.center/index.php/2709-4685/article/view/3099
21. E.A. Khanmamedova, Analysis of electrical conductivity in nanotransistor structures with graphene oxide nanofibers, V International Scientific and Practical Conference «Theoretical and empirical scientific research: concept and trends» p.-152-155, June 23, 2023; Oxford, UK. https://archive.logos-science.com/index.php/conference-proceedings/issue/view/12/12
22. E.A. Khanmamedova, R.G. Abaszade, R.Y. Safarov, R.A. Namazov Graphene-based transistors, Ecoenergetics, №2, pp.52-57, 2023. http://ieeacademy.org/wp-content/uploads/2023/06/Ecoenergetic_-N2-2023-full.pdf
23. E.A. Khanmamadova Dıodes made from carbon nanotubes, International scientific journal «Grail of Science» |No29(July, 2023), p. 225-229. https://archive.journal-grail.science/index.php/2710-3056/article/view/1447
24. R.G. Abaszade, A.G. Mammadov, V.O. Kotsyubynsky, E.Y. Gur, I.Y. Bayramov, E.A. Khanmamadova,O.A. Kapush, Photoconductivity of carbon nanotubes, International Journal on Technical and Physical Problems of Engineering, Vol.14, №3, pp.155-160, 2022. http://www.iotpe.com/IJTPE/IJTPE-2022/IJTPE-Issue52-Vol14-No3-Sep2022/21-IJTPE-Issue52-Vol14-No3-Sep2022-pp155-160.pdf
25. E.A. Khanmamedova, Thermal processing analysis of graphene oxide, april 28, 2023; seoul, south korea: ii international scientific and practical conference «theoretical and practical aspects of modern scientific Research» https://archive.logos-science.com/index.php/conference-proceedings/article/view/714
26. L.S. Anthony, M. Vasudevan, V. Perumal, M. Ovinis, P.B. Raja, Edison, T.N.J.I., Bioresource-derived polymer composites for energy storage applications: brief review, J. Environ. Chem. Eng. 9, 105832, 2021.
27. L. Li, L. Hou, Cheng, J., Simmons, T., Zhang, F., Zhang, L.T., Linhardt, R.J., Koratkar, N. (2018). A flexible carbon/sulfur-cellulose core-shell structure for advanced lithium–sulfur batteries, Energy Storage Mater.
28. E.A. Khanmamedova Schematic representation of the preparation of graphene oxide, Ecoenergetics, №1, pp.63-67, 2023. http://ieeacademy.org/wp-content/uploads/2023/03/Ecoenergetics-N1-2023-1.pdf
29. J. Liu, S. Fu, B. Yuan, Z. Deng, M. Shen, Facile synthesis of graphene oxide and its reduction. Journal of Materials Chemistry, 20(35), pp.7491-7496, 2010; https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6628170/
30. E.A. Khanmamedova, Mathematical model analysis of graphene oxide thermal development, no. 26 (2023): i cisp conference «Scientific vector of various sphere' development: reality and future trends» https://archive.journal-grail.science/index.php/2710-3056/article/view/1145
31. P. Avouris, Graphene: Electronic and Photonic Properties and Devices. Nano Letters, 10(11), 4285–4294, 2010; https://pubs.acs.org/doi/abs/10.1021/nl102824h
32. E.A. Khanmamedova, X-ray analysis of graphene based materials, Proceedings of the 7th International Scientific and Practical Conference «Current Issues and Prospects for The Development of Scientific Research» (April 19-20, 2023). Orléans, France https://archive.interconf.center/index.php/2709-4685/article/view/3100
33. Y. Zhang, Y.W. Tan, H.L. Stormer, P. Kim, Experimental observation of the quantum Hall effect and Berry's phase in graphene. Nature, 438(7065), pp.201-204, 2005; https://arxiv.org/abs/cond-mat/0509355
34. F. Kim, L.J. Cote, J. Huang, Graphene Oxide: Surface Activity and Two-Dimensional Assembly. Advanced Materials, 22(17), 1954–1958, 2012;

https://scholar.google.com/citations?hl=th&user=sbfLJqUAAAAJ&view_op=list_works&sortby=pubdate

35. L. Ju, B. Geng, J. Horng, C. Girit, M. Martin, Z. Hao, H.A. Bechtel, X. Liang, A. Zettl, Y. R. Shen, F. Wang, Graphene plasmonics for tunable terahertz metamaterials. Nature nanotechnology, 6(10), pp.630-634, 2011; https://pubmed.ncbi.nlm.nih.gov/21892164/
36. M.I. Katsnelson, A.K. Geim, Electron scattering on microscopic corrugations in graphene. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 366(1863), pp.195-204, 2008; https://www.jstor.org/stable/i25190665
37. A. Peigney, C. Laurent, E. Flahaut, R.R. Bacsa, A. Rousset, Specific surface area of carbon nanotubes and bundles of carbon nanotubes. Carbon, 39(4), pp.507-514, 2001; https://www.scirp.org/(S(351jmbntv-nsjt1aadkposzje))/reference/referencespapers.aspx?referenceid=1135853
38. W. Xiaohan, Jinwon, J., Yanqun, S., Jingang, L., Hongjie, Z., Zhibin, H., Yonghao, N., (2024). Starting materials, processes and characteristics of bio-based foams: A review, Journal of Bioresources and Bioproducts 9, 160–173.
39. E.A. Khanmamedova, X-ray analysis of graphene based materials, 9th International Scientific and Practical Conference «Theory and practıce of scıence: key aspects» February 19-20, 2024 Rome, Italy pp.599-603, https://archive.interconf.center/index.php/2709-4685/article/view/3100
40. R.G. Abaszade, A.G. Mammadov, E.A. Khanmamedova, F.G. Aliyev, V.O. Kotsyubynsky, E. Gür, B.D. Soltabayev, T.O. Margitich, M.O. Stetsenko, A. Singh, S. Arya, Photoconductivity of functionalized carbon nanotubes, Digest Journal of Nanomaterials & Biostructures (DJNB), 2024, Vol 19, Issue 2, p837, 2024; https://openurl.ebsco.com/EPDB%3Agcd%3A4%3A22925460/detailv2?sid=ebsco%3Aplink%3Ascholar&id=ebsco%3Agcd%3A178220998&crl=c&link_origin=scholar.google.com
41. A. Grunwald, Assigning meaning to NEST by technology futures: extended responsibility of technology assessment in RRI. Journal of Responsible Innovation 4 (2), 2017.
42. D.H. Guston, Understanding ‘anticipatory governance. Soc. Stud. Sci. 44 (2), pp.218–242, 2014.
43. H.S. Toogood, A.N. Cheallaigh, S. Tait, D.J. Mansell, A. Jervis, A. Lygidakis, Enzymatic menthol production: one-pot approach using engineered Escherichia coli. ACS Synth. Biol. 4 (10), pp.1112–1123, 2015.
44. J.R. Moreira, S.A. Pacca, J. Goldemberg, The role of biomass in meeting the Paris agreement, IOP Conf. Series: Earth and Environmental Science 354, 012107, 2019.
45. Sh. Ahmed, P. Sharma, S. Bairagi, N.P. Rumjitf, Sh. Garg, Ali, A., Lai, Ch.W., Mousavi, S.M., Hashemi, S.A., Hussain, Ch.M. Nature-derived polymers and their composites for energy depository applications in batteries and supercapacitors: Advances, prospects and sustainability, Journal of Energy Storage 66, 107391, 2023.
46. Z. Du, Y. Su, Y. Qu, L. Zhao, X. Jia, Y. Mo, F. Yu, J. Du, Y. Chen, A mechanically robust, biodegradable and high-performance cellulose gel membrane as gel polymer electrolyte of lithium-ion battery, Electrochim. Acta, 2019.
47. M.E. Morales, M.A. Ruiz, Microencapsulation of probiotic cells: applications in nutraceutic and food industry, Nutraceuticals, 2016.


ECO
ENERGETIKA
ENERGETICS