CHEMISTRY & CHEMICAL TECHNOLOGY

Chem. Chem. Technol., 2025,
Vol. 19, No. 3, pp. 503–510

Chemistry

OBTAINING AN ECO-FRIENDLY BIOCOMPOSITE BASED ON WALNUT SHELL FOR USE IN FURNITURE PRODUCTION

Lali Tabatadze[1,✉], Darejan Iremashvili[1], David Gventsadze[2], Manana Berulava[1], Natia Shengelia[1]

https://doi.org/10.23939/chcht19.03.503

Abstract. Polymer composite materials are modern industrial products containing reinforcing fillers obtained from renewable agricultural and plant raw materials. The results of this study showed the effect of a natural filler consisting of walnut shells on the physical and mechanical properties of biomaterials. Using simple technology and an environmentally friendly approach, a formaldehyde-free biomaterial based on polypropylene modified with tetraethyl orthosilicate (TEOS), was obtained. The effect of processing parameters (Relative density, Compression strength, Bending strength, Impact viscosity, Water absorption) on the physical and mechanical properties of biomaterials was observed. As a result of modification with TEOS, the mechanical characteristics of biomaterials, as well as their operational properties, were improved. The optimal composition of the developed modified biocomposites is 60 wt.%, while the strength and impact strength indicators are maximum and are respectively: 65.87 MPa, 43.25 MPa and 6.8 kJ/m^2, which allows the use of the developed composites for the manufacture of unloaded furniture elements. The effect of the new material on the biological system was studied. The obtained result showed that the biocomposite did not affect the total number of leukocytes in the peripheral blood, and did not change the histoarchitecture of the liver and brain tissues in adult white mice.

Keywords: biocomposite, cellulose, TEOS, environmental protection, biological research, FTIR spectroscopy.

Introduction

The unique structure of cellulose, consisting exclusively of equatorial OH groups and glycoside bonds, provides cellulose with exceptional physical and chemical properties, such as high mechanical strength and insolubility in common solvents.[7] Environmental pollution is one of the most important problems affecting the modern world. According to the United Nations, 19–23 million tons of plastic waste enter rivers, seas and oceans every year, exerting an irreversible negative impact on ecosystems. Household and industrial products derived from polyolefines do not decompose in the atmosphere; they slowly disintegrate into small fragments of micro plastics, which have been found in drinking water and the human body, as well as in fish. They damage the endocrine system, cause infertility and hormonal imbalances.

The production of cellulosic materials based on renewable biomass is a promising strategy to protect the environment. The solution to the above problem requires the development of new technologies that can reduce the amount of polymer waste in the environment by 50-60% and convert biomaterials into biodegradable ones; this could offer a guarantee for environmental protection and the prevention of pollution on a global scale.

In the consumer market, Decking derived from raw wood materials and various building materials still contain phenolic compounds and formaldehyde; therefore, they are hazardous to health.[8-10] Criteria for the limitation and regulation of formaldehyde emissions from wood-based materials were established in 1981 in Germany and Denmark. The first regulations in the United States followed in 1985. World health experts have found that products containing formaldehyde can cause depression and respiratory problems and damage the nervous system. Several leading countries around the world have adopted standards for the removal of formaldehyde from composite polymer materials. Scientific works[11-15] of various authors confirm that the use of polyolefin and cellulose-based fillers in the production of thermoplastic composites with bio fillers allows solving the problems of waste disposal. The works show the development of composite materials based on recycled polypropylene with walnut shell waste and various plant fillers, which can be used in both automotive and construction industries.

[1] Sokhumi State University, Faculty of Natural Sciences, Mathematics, Technology and Pharmacy. Department of Chemistry. Tbilisi, 0186, Georgia
[2] Iv. Javakhishvili Tbilisi State University, R. Agladze Institute of Inorganic Chemistry and Electrochemistry, Tbilisi 0186, Georgia
✉ *l.tabatadze@sou.edu.ge*

A new, aldehyde-free biomaterial was produced for the first time by using polymer waste and renewable raw nut materials of natural origin (walnut shell flour). An industrial polymer was chosen as a binder, namely secondary isotactic polypropylene, which is a universal plastic material that is light, cheap, impact-resistant and wear-resistant, with good insulating properties, among others. It is important that the properties of biomaterials obtained from recycled and primary polypropylene are not significantly different.

Biocomposites were made from polymer waste – in the form of walnut shell flour, where the percentage of cellulose is 35%, lignin – 41%, the rest is hemicellulose and pectins. Cellulose acts as a natural structural material, which provides high mechanical strength and has excellent mechanical properties, whereas lignin reduces water absorption and increases heat resistance. A large number of shells are collected and disposed via burning or by burying them in the ground, which pollutes the environment. However, due to the chemical composition of the shell, it is rarely used in animal feed or as an additive in pharmaceutical medicine.

This work discusses the development of new, safe for health, unmodified and modified via TEOS biomaterials produced using a simple technology of hot pressing.

2. Experimental

2.1. Materials

Isotactic polypropylene powder ("Polyvini", Rustavi, Georgia) was used as received. TEOS liquid (China) was purchased from Aldrich. The walnut shells were collected from a Georgian walnut processing plant.

2.2. Methods

Samples for testing were produced via hot pressing in appropriate molds at a temperature of 170 ^{0}C and pressure of 15 MPa, with a holding period of 10 minutes. The obtained samples were assessed to measure their relative density, compression strength, bending strength, impact viscosity and water absorption. The water absorption of all specimens was measured according to ISO 62 2002, and strength to Compression strength was determined for specimens with a 10 mm diameter and 20 mm height, according to ISO 604 2002. Flexural strength and Impact strength were measured by the "Izod method" according to the ISTM D256 standard on a "Distant" device with sample sizes of 15x10 (1.5-4.5) mm.

The rest of the walnut shells were washed and then dried at 120 ^{0}C for 3 hours, after which they were crushed on a "Vibratory Disc Mill RS - Retsch" tool (Fig. 1a). The grain sizes of the sifted walnut shells were 15-100 μm. To prepare test samples of the biomaterial, the walnut shells were pretreated via crushing, grinding, sifting and drying (Fig. 1a-c). To produce 40, 60 and 80% unmodified and modified test samples, the hot-pressing method was used. This method involved mechanical mixing of 10-500 μm isotactic polypropylene grains with dried, crushed and ground walnut shells. The mixture was mixed in a propeller mill (for 2-3 minutes). In order to improve the physical and mechanical properties, the developed biomaterials were modified 5 wt.% with TEOS liquid.

a b c

Fig. 1. Processing of walnut shells: a) crushing, b) grinding, c) sifting

The modification is carried out as follows: dilute 5 wt. % of TEOS liquid, dissolving it in toluene (at the rate of 10 ml per 95 g of walnut shell). The diluted TEOS liquid is added to the walnut shell flour, mixed thoroughly, dried at 70 ^{0}C, and then mixed with polypropylene powder in a propeller mill.

The elemental analysis of the samples was carried out on a JSM-6510LV scanning electron microscope

(JEOL), equipped with an X-Max N energy-dispersive micro-X-ray spectral analyzer from Oxford Instruments. For elemental analysis the electron imaging of the sample surface was performed using secondary electrons (SEI) at an accelerating voltage of 20 kV. The distance from the sample surface was 15 mm.

The chemical composition of unmodified and modified biomaterials was studied using a Fourier transform infrared spectroscopy. FTIR spectroscopic investigations were conducted on a Shimadzu IRAffinity-1S FTIR Fourier Transform Infrared Spectrophotometer. The wavelength was 4000-700 cm^{-1} (scan 32, resolution 4 cm^{-1}), band intensities were denominated in transmittance and the mode was UATR.

Changes in the tissue histoarchitecture were assessed via the microscopic observation of paraffin-embedded tissue sections. A Guryev camera was used to count the total number of leukocytes in the blood of young mice[16].

To examine the early effects of exposure, the influence of the biomaterial for 40 days was studied.

In order to examine the tissues (liver) under a light microscope, the materials were fixed in the 4% formaldehyde solution prepared on the Na/K phosphate buffer. Dehydration of the material took place in an increasing range of alcohols of different concentrations. Tissues were embedded in a wax-paraffin mixture. 5-7 µm thick slices were stained with hematoxylin-eosin. Tissue samples were studied under a light microscope (Zeiss Primo Star, Germany).

Determination of the total number of leukocytes in peripheral blood: 20 µl of blood sample taken from the tail of animals anesthetized with diethyl ether was dissolved in 400 µl of 3% acetic acid and kept at room temperature for 20 min. A certain volume of the sample was placed in a Goryaev chamber, the number of leukocytes were counted according to a standard protocol using a light microscope (at low magnification, lens 20, eyepiece 10).

Statistical analysis. The data are expressed as mean ± SD. Students' t-test was used for comparison among the different groups. $P<0.05$ was considered statistically significant.

To assess the effectiveness of this composite, experimental animals were divided into 2 groups:

1. Control group - intact animals.
2. Experimental group - animals kept in cages covered with the test composite for 40 days.

3. Results and Discussion

3.1. The physical and mechanical characteristics of unmodified and modified samples

Table 1 shows the physical and mechanical characteristics of the experimental samples of the unmodified and modified biomaterials, namely their relative density, compression strength, bending strength, impact viscosity, water absorption. We determined the technological mode of production. Table 1 shows that the experimental samples were characterized by lightness (their weight range was 1035-1385). Compared to the unfilled polymer, the filled biomaterials had increased compressive and bending strength and reduced impact toughness. The modified samples were relatively light.

Table 1. The physical and mechanical characteristics of unmodified and modified samples

Samples	Relative density, kg/m^3	Compression strength, MPa	Bending strength, MPa	Impact viscosity, kJ/m^2	Water absorption,%	Acceptance of technical regime
Unfilled PP	915	42.60	28.00	25.0	0.00	15 MPa 160±5^{0}C 10 min
Unmodified PP + 40 wt.%	1035	64.7	40.50	4.5	0.15	
Unmodifie PP + 60 wt.%	1137	59.56	38.70	4.4	1.40	
Unmodified PP + 80 wt.%	1385	35.40	32.30	3.5	1.84	
Modified PP + 40 wt.%	1030	64.2	40.60	5.7	0.1	
Modified PP + 60 wt.%	1134	65.87	43.25	6.8	1.0	
Modified PP + 80 wt.%	1370	41.3	36.21	4.2	1.35	

With an increasing percentage of filling, the compressive strength, bending strength and impact toughness decreased; at the same time, it was seen that the modification increased the strength and reduced the water absorption. It is evident that the optimal composition of the developed modified biocomposites is 60 wt.%, while the strength and impact indices are the highest and amount to: 65.87 MPa, 43.25 MPa and 6.8 kJ/m^2, and it is possible that the developed composites can be used for the manufacture of unloaded furniture elements. As for water absorption, the composite we obtained with a filler content of 80 wt.% (1.35%) is lower than the values given in the authors' work [13] for composites with the same filling, which amount to more than 2%.

3.2. The chemical composition study of the 60 wt. % modified biocomposites using FTIR

The chemical composition of the 60 wt. % modified biomaterial was studied using the Fourier transform infrared spectroscopy. In the FTIR spectrum, shown in Fig. 2 (cm^{-1}, γ, m. n.), there are no characteristic absorption bands of allyl groups (-CH_2–CH=CH_2) in the region of 1647 cm^{-1} and absorption open chain are observed in the region of 770-999.32 cm^{-1} characteristic of polypropylene. The absorption band in the region of 2838.21–2917.24 cm^{-1} was characteristic of the valence bond of the –CH_2– group in cellulose (standing at the carbon atom C6) and 2950.30 cm^{-1} (CH_3–) group. Impurities of aromatic and aliphatic nitriles were observed in the regions of 1595.14 cm^{-1} (C=C) and 2300-2200 cm^{-1}. We also observed the values of deformation vibrations in the region of 1375.27 cm^{-1} and 1457.19 cm^{-1} are characteristic of (-CH_2-) and (-CH_3) groups; 1734.54 cm^{-1} was a characteristic absorption band for the (C=O) group. In the region of 1100.79 cm^{-1}, a characteristic absorption band of the (C-O-C) bond was observed, and in the region of 1090 cm^{-1}, an absorption band of the (Si-O-C) bond was found.

3.3. The elemental analysis of unmodified PP + 60 wt. % and modified PP + 60 wt. % biomaterial samples

The elemental analysis of the not modified PP + 60 wt. % and modified PP + 60 wt. % biomaterial samples (Figs. 3, 4 and 5, 6, respectively) was performed using a scanning electron microscope. The results of the radiographic examination are shown in Figs. 4, 6, which present the highest Au and carbon content and the corresponding percentages of the elements present, including Si. In order to reduce the surface charge, the samples were coated with a layer of gold, approximately 10 nm thick, which explains the high intensity of the Au peak in the elemental analysis data shown in Fig. 4 and 6. The samples were coated using a JEC-3000FC vacuum sputtering system from JEOL.

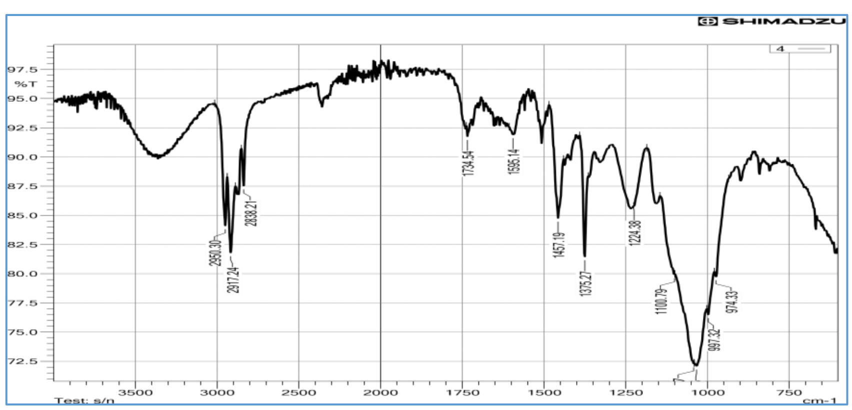


Fig. 2. FTIR spectrum of the 60 wt. % modified sample

3.4. Biological investigation of biocomposite for health safety

In order to determine the material's safety on health, studies were conducted on living organisms (mice) at the Biology Department, Faculty of Exact and Natural Sciences, Iv. Javakhishvili Tbilisi State University. This study was conducted on white adult mice (25–30 g). The following materials were used for the study: walnut shells modified with TEOS and the tissue samples of adult white mice (blood, liver and brain). Changes in the hepatic and brain histoarchitecture were assessed via the microscopic observation of paraffin-embedded tissue sections collected after 40 days of exposed biomaterial. A Guryev camera was used to count the total number of leukocytes in the blood. The duration of the experiment was 40 days (Fig. 7).

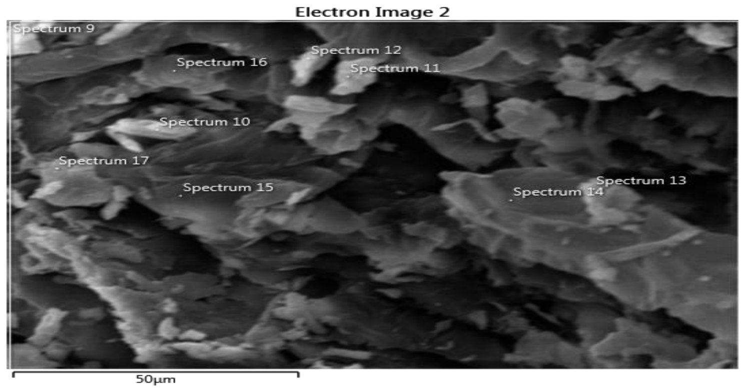


Fig. 3. Scanning electron microscope image of 60 wt. % unmodified biomaterials

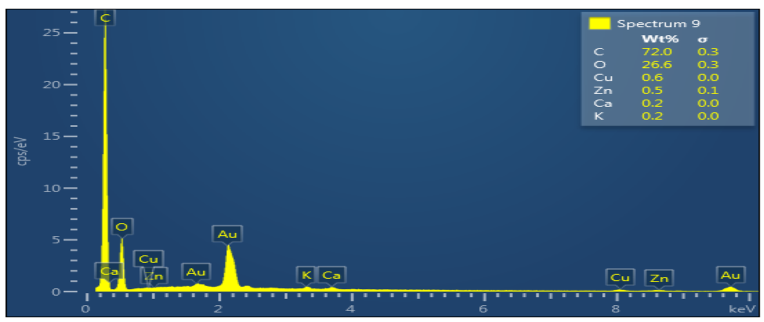


Fig. 4. Elemental analysis of 60 wt. % unmodified biomaterials

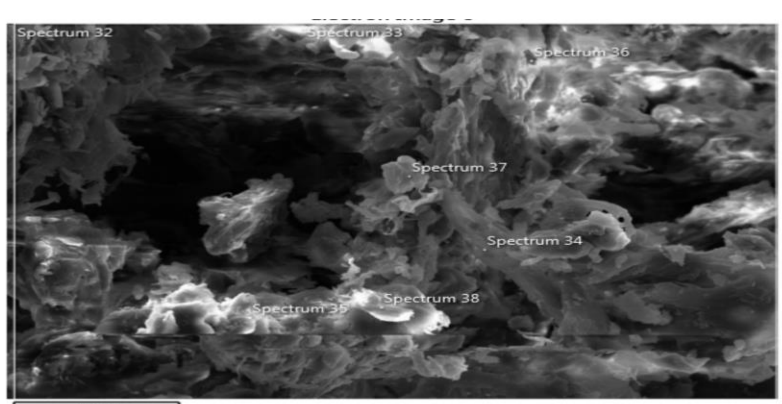


Fig. 5. Scanning electron microscope image of 60 wt. % modified biomaterials

Fig. 6. Elemental analysis of 60 wt. % modified biomaterials

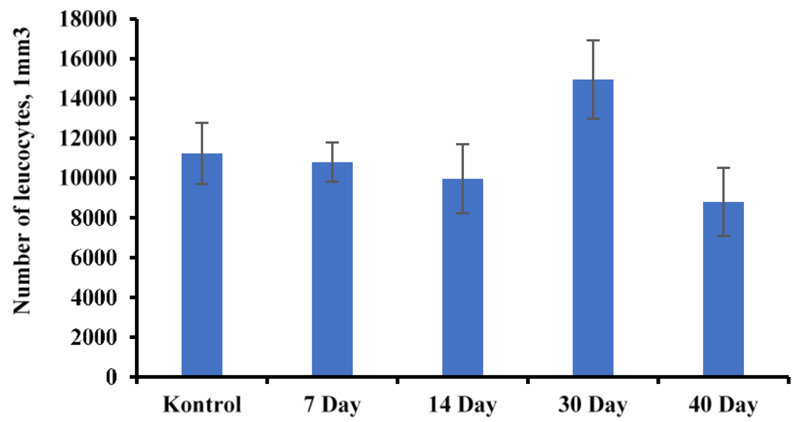
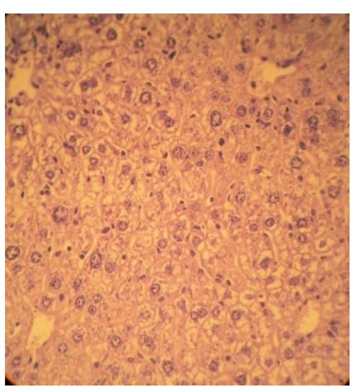
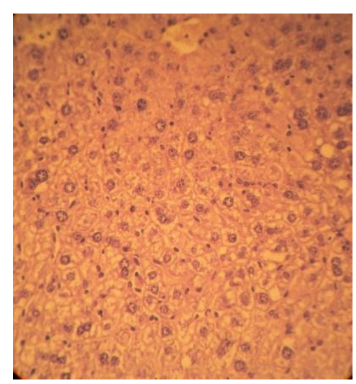


Fig. 7. The effect of the 60 wt. % modified biomaterial sample containing walnut shells on the total number of leukocytes in the peripheral blood of adult white mice ($p>0.5$)

Fig. 7 clearly shows that the new composite of walnut shells has not changed the total number of leukocytes in the peripheral blood of adult white mice. In parallel, the histoarchitectonics of liver and brain tissues of the animals were studied. Fig. 8 shows micrographs of the histo-architectonics of the liver of control and experimental groups of animals. It is well distinguished the radial direction of trabeculae to the central vein, with sinusoidal capillaries. Fig. 9 shows micrographs of brain tissue of both groups' animals. Based on the obtained results, it should be noted that morphological changes in the liver and brain tissues of the experimental group animals were not observed.

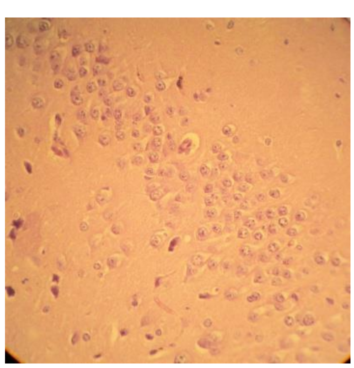


a

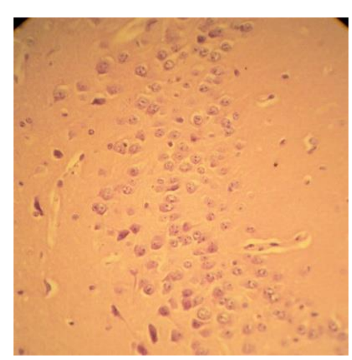


b

Fig. 8. Liver tissue histoarchitechture of adult white mice. a – control; b – experimental. X400, H&E



a



b

Fig. 9. Brain tissue histoarchitechture of adult white mice. a – control; b – experimental. X400, H&E

4. Conclusions

New, safe biomaterials without phenol and formaldehyde were obtained based on renewable plant materials (walnut shells) and recycled waste - polyolefins. Their physical and mechanical properties were studied. The chemical composition of the 60 wt. % modified biomaterial was studied using the Fourier transform infrared spectroscopy. Observed in the region of 770-999.32 cm^{-1} characteristic of polypropylene and in the region of 1090 cm^{-1}, an absorption band of the (Si-O-C) bond was found. The experiments showed that this biomaterial modified with TEOS, based on walnut shells and isotactic polypropylene residues and caused no change in the total number of leukocytes in the blood of white mice. Moreover, the biomaterial tiles used in the experiments did not have a negative effect on the morpho-functional activity of various tissue types in adult white mice.

Thus, the biomaterial modified with TEOS and based on walnut shells and isotactic polypropylene residues is not cytotoxic and is environmentally safe. This expands the possibilities for the widespread use of biomaterials, especially in furniture, both automotive and construction industries. Moreover, from the perspective of conversion technologies, this simple and low-cost method opens up unlimited possibilities to obtain new materials that are safe for health.

Author Contributions: All authors reviewed the manuscript and contributed equally. All authors have read and agreed with the published version of the manuscript.

Funding: This research was funded by the Ministry of Education, Science and Youth of Georgia, «Competition Innovation Fund (CIF)», 2nd grant project No. CIF-2-2024-08 agreement.

http://iiq.gov.ge/ge/2024/04/%e1%83%99%e1%83%9d%e1%83%9c%e1

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The financial support of the Competition Innovation Fund (CIF), of the Ministry of Education, Science and Youth of Georgia» (Project N CIF-2-2024-08)

Conflicts of Interest: The authors declare no conflicts of interest.

The funders did not take part in the design of the study; in the collection, analyses, or interpretation of data; in writing of the manuscript, or in the decision to publish the results.

References

[1] Di, X.; Liang, X.; Shen, Ch.; Pei, Yu.; Wu, B.; He, Zh. Carbohydrates Used in Polymeric Systems for Drug Delivery: From Structures to Applications. *Pharmaceutics* **2022,** *14*, 739. https://doi.org/10.3390/pharmaceutics14040739

[2] Wafiroh, S.; Abdulloh, A.; Widati, A. Cellulose Acetate Hollow Fiber Membranes from Banana Stem Fibers Coated by TiO_2 for Degradation of Waste Textile Dye. *Chem. Chem. Technol.* **2021**, *15*, 291–298. https://doi.org/10.23939/chcht15.02.291

[3] Sidamonidze, N.; Tabatadze, L.; Vardiashvili, R.; Nutsubidze, M.; Iremashvili, D.; Chachua, E.; Shengelia, N. Hydrosulphurisation Reactions of Allyl Derivatives of Altropyranose with Mercaptans. *Oxid. Commun*. **2023***, 47*, 337–344. https://scibulcom.net/en/journal/0209-4541/issue/2023-46-2/

[4] Pachulia, Z.; Shengelia, N.; Tabatadze, L.; Gakhokidze, R. Modeling of the Synthesis of Sulfanilamide Monoglucoside by Quantum-Chemical Method. *Bulletin of the Georgian National Academy of Sciences **2016**, 10*, 33–36. http://science.org.ge/bnas/vol-10-4.html

[5] Sidamonidze, N.; Tabatadze, L.; Vardiashvili, R. Condensation Reactions of 1-Chloro-2,3,4-tri-O-acetyl-α-L-Arabinopyranose and 1-Chloro-2,3,4-tri-O-acetyl-α-L-Rhamnopyranose with α-Pyrrolidone and Caprolactams. *Oxid. Commun.* **2022,** *45*, 628–634. https://scibulcom.net/en/journal/0209-4541/issue/2022-45-4/

[6] Sidamonidze, N.; Gakhokidze, R.; Vardiashvili, R.; Gelovani, T.; Tabatadze, L. Synthesis and Biological Activity of some Derivatives of N-Glycosylamines. *Oxid. Commun.* **2023**, *46*, 87–95. https://scibulcom.net/en/journal/0209-4541/issue/2023-46-1/

[7] Mtchedlishvili, M.; Tabatadze, L.; Gventsadze, D.; Lezhava, T.; Gventsadze, L.; Iremashvili, D.; Shonia, T. Technological Aspects of Biopolymers Based on Yucca Gloriosa Fiber. *Bulletin of the Georgian National Academy of Sciences* **2024**, *18*, 138–144. http://science.org.ge/bnas/vol-18-4.html

[8] Chen, Ch.; Xu, C.; Zhai, J.; Zhao, Ch.; Ma, Yu.; Yang, W. Low-Cost and Formaldehyde-Free Wood Adhesive Based on Water-Soluble Olefin-Maleamic Acid Copolymers. *Ind. Eng. Chem. Res.* **2023**, *62*, 20547–20555. https://doi.org/10.1021/acs.iecr.3c01968

[9] Salthammer, T.; Mentese, S.; Marutzky, R. Formaldehyde in the Indoor Environment. *Chem Rev*. **2010**, *110*, 2536–2572. https://pubs.acs.org/doi/10.1021/cr800399g

[10] Tatrishvili1, T.; Mukbaniani, O.; Kvnikadze, N.; Chikhladze, Sh. Eco-Friendly Bamboo-Based Composites. *Chem. Chem. Technol.* **2024**, *18*, 44–56. https://doi.org/10.23939/chcht18.01.044

[11] Obidiegwu, M.; Nwanonenyi S.; Eze I.; Egbuna I. The Effect of Walnut Shell Powder on the Properties of Polypropylene Filled Composite. *The International Asian Research Journal* **2014**, *2*, 22–29. https://www.researchgate.net/publication/354684222

[12] Al-Sarraf, M. A. Sustainable and Environmentally Friendly Composites: Development of Walnut Shell Powder-Reinforced Polypropylene Composites for Potential Automotive Applications. *J. Mech. Behav. Mater*. **2024**, *33*, 20240017. https://doi.org/10.1515/jmbm-2024-0017

[13] Danchenko, Y.; Kariev, A.; Lebedev, V.; Barabash, E.; Obizhenko, T. Physic-Mechanical Properties of Composites Based on Secondary Polypropylene and Dispersed of Plant Waste. *Mater. Sci. Forum* **2020**, *1006*, 227–232. https://doi.org/10.4028/www.scientific.net/MSF.1006.227

[14] Herasymenko, V.; Kariev, A.; Balandaieva, L.; Lebedev, V.; Vynohradov, V. Construction Composites Based on Secondary Thermoplastics and Manufacturing Waste. *IOP Conference Series: Earth and Environ. Sci*. **2024**, *1376*, 012011. http://dx.doi.org/10.1088/1755-1315/1376/1/012011

[15] Turkadze, Ts.; Gventsadze, D.; Mumladze, T.; Gorgodze, G.; Bochoidze, I. Characterization of Polypropylene Composite Reinforced on Bio-waste from the Production of Tung Oil. *Environ. Res. Eng. Manage.* **2023**, *79*, 29–38. https://erem.ktu.lt/index.php/erem/article/view/33393
[16] Nakhutsrishvili, G.; Berulava, M.; Tavdishvili, E.; Londaridze, L.; Dzidziguri, D. Study of Possible Negative Impact of a New Wood Composite Containing Triethoxysilylated Styrene on a Living System in Experiment. In *Advanced Polymer Structures*. *Chemistry for Engineering Applications*; Mukbaniani, O.; Tatrishvili, T.; Abadie, M.J.M., Eds.; Apple Academic Press: New York, 2023. https://doi.org/10.1201/9781003352181

This research was Carried out within the framework of the project by the Ministry of Education, Science and Youth of Georgia, «Competition Innovation Fund (CIF)», 2nd grant project No. CIF-2-2024-08 agreement.

Received: January 10, 2025 / Revised: March 29, 2025 / Accepted: April 16, 2025

ОТРИМАННЯ ЕКОЛОГІЧНО ЧИСТОГО БІОКОМПОЗИТУ НА ОСНОВІ ШКАРАЛУПИ ВОЛОСЬКОГО ГОРІХА ДЛЯ ВИКОРИСТАННЯ У ВИРОБНИЦТВІ МЕБЛІВ

Анотація. *Полімерні композитні матеріали – це сучасні промислові продукти, що містять армувальні наповники, отримані з відновлюваної сільськогосподарської та рослинної сировини. Результати цього дослідження показали вплив натурального наповника, що складається зі шкаралупи волоських горіхів, на фізико-механічні властивості біоматеріалів. Використовуючи просту технологію й екологічно чистий підхід, було отримано біоматеріал без формальдегіду на основі поліпропілену, модифікованого тетраетилортосилікатом (ТЕОС). Визначали вплив параметрів обробки (відносна густина, міцність на стиск, міцність на вигин, ударна в'язкість, водопоглинання) на фізико-механічні властивості біоматеріалів. У результаті модифікації ТЕОС покращилися механічні характеристики біоматеріалів, а також їхні експлуатаційні властивості. Оптимальний склад розроблених модифікованих біокомпозитів становить 60 мас.%, при цьому показники міцності й ударної в'язкості є максимальними та становлять відповідно: 65,87 МПа, 43,25 МПа і 6,8 кДж/м^2, що дає змогу використовувати розроблені композити для виготовлення ненавантажених елементів меблів. Було досліджено вплив нового матеріалу на біологічну систему. Отриманий результат показав, що біокомпозит не впливав на загальну кількість лейкоцитів у периферичній крові, а також не змінював гістоархітектуру тканин печінки та мозку в дорослих білих мишей.*

Ключові слова: *біокомпозит, целюлоза, ТЕОС, захист навколишнього середовища, біологічні дослідження, FTIR спектроскопія.*