Scientific Journals
of the Maritime University of Szczecin

Zeszyty Naukowe
Politechniki Morskiej w Szczecinie

2024, 78 (150), 15–21
ISSN 2392-0378 (Online)
DOI: 10.17402/603

Received: 16.04.2024
Accepted: 26.04.2024
Published: 30.06.2024

Application properties and microscopic analysis of elastomer samples cross-linked by gamma radiation

Jasminka Bonato

https://orcid.org/0000-0003-1448-3296

University of Rijeka, Faculty of Maritime Studies
2 Studentska St., 51000 Rijeka, Croatia
E-mail: jasminka.bonato@pfri.uniri.hr

Keywords: natural rubber, application characteristics, gamma radiation, microscopic analysis, SEM, EDX

JEL Classification: L74, L79, O3

Abstract

Natural rubber is an important industrial material derived from caoutchouc trees (*Hevea Brasiliensis*). By chemical composition, it is a polymer material that is mostly *cis*-1,4-polyisoprene. It falls into the category of elastomers, which enables its wide usage due to its specific characteristics. Polymer materials include plastic, rubber, and glue and are the most important technical materials. Rubbers are used in the production of conveyor belts, shock absorbers, coatings, fenders, engines, and device parts. They are also used in composite materials such as threads, particles, and matrix materials. By analyzing the properties of natural rubber, the subject of the research is defined, i.e., the characterization of natural rubber samples and their connection with macroscopic properties. In accordance with the subject of the research, in this paper, tests are carried out on samples of natural rubber, which are obtained in the form of thin films from latex and cross-linked by gamma radiation. A total dose of 300 kGy is applied to the samples in the state of uniaxial deformation. In this sense, a hypothesis is put forward that involves examining the influence of radiation dose on the morphology of natural rubber samples using scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDX). The investigation aims to emphasize the importance of the method in acquiring a comprehensive characterization of the material samples, which are used both in maritime areas and in other fields of application.

Introduction

The research of the structure of materials and establishing relations with macroscopic characteristics is of substantial significance for applications (Roland, 2005). Conditions of the applications define the demanded characteristics: mechanical, electric, thermal, magnetic, and optical. These characteristics refer to materials of a certain structure and chemical composition (Table 1).

There are a significant number of various polymer characteristics, such as their resistance to chemicals and corrosion. They are good heat and electricity insulators as well (Pintaric, 2009). The disadvantages refer to their low strength, high inflammability, and proneness to aging and decomposition. Various supplements that improve one or more of their characteristics affect the polymer properties and structures, and, thus, polymer materials used in industry are obtained (Roslim et al., 2015).

In the maritime area, polymer materials are not only used as construction materials (Esih, 2003) but also in coatings. Many products based on natural rubber are used in seamanship to protect offshore structures and the outer hull of the vessel. They are also used to protect internal tanks from sea corrosion due to their ability to fill tank damages and cracks (Kendrick & Caccese, 2005). Polymers are macromolecular compounds made of a large number of basic units, which are interconnected by covalent

Table 1. Display of important engineering materials (Čatić et al., 2010)

Metal materials	Non-metallic inorganic materials	Polymer materials	Compound materials (composites)
Technical metals: Fe, Cu, Al, Ni, Ti	Ceramic: Silicate: clay, porcelain, glass ceramics	Thermoplastics: PE, PVC, PP, PA, POM	Reinforced by fibers: GFK, CFK, PFK
Other metals: Zr, V, Nb, Ta, Cr, Mo, W	Oxide: Al_2O_3, ZrO_2	Duroplasts: PF, UP, EP	Reinforced by particles: TD-Ni
Precious metals: Ag, Pt, Au, Pd	Non-oxide: SiC, Si_3N_4, BN, C	Elastomers: NR, SBR, NBR, FPM	
	Glass: Silicate glass		
	Binders: cement, lime, gypsum		

bonds. Types of chain molecules affect the behavior of materials when heated. They also define their application characteristics, according to which polymers are divided into three groups: plastomers, duromers, and elastomers (Janović, 1997)**.** Natural rubber shows the quality of elasticity and, typically, is an elastomer. Elastomer characteristics depend on the characteristics of basic polymer chains and the presence of intermolecular covalent bonds. They can obtain multiple increases in length at room temperature. After the stretching period, they return to their starting length. Natural rubber, just like synthetic elastomers, has to be subjected to networking. That is, when the cross-linking of chain molecules occurs (Billmeyer, 1984), and also the desired usage characteristics of the materials are obtained. Material treated in such a way shows the appropriate elasticity, breaking strength, toughness, and the quality of being wearproof (Valić et al., 1991; Bokobza, 2005). Networking can be performed in the state of uniaxial material deformation (Miyamoto, Yamao & Sekimoto, 2003), for example, via a constant application of an outer mechanical force (Toki et al., 2002; Rault et al., 2006a). Rubber products that are no longer fit for use are a great environmental problem. Their combustion produces large amounts of gases (i.e., sulfur dioxide and carbon dioxide) and represents a sizeable threat to the environment. Therefore, this paper deals with natural rubber vulcanized by -radiation because it does not threaten the environment or contain sulfur. Scanning electron microscopy (SEM) is one of the most suitable methods to analyze and characterize the morphology of a material (Sellaro, Sarver & Baxter, 2015). This paper presents the methodology that uses scanning electron microscopy equipped with energetically dispersive X-rays (Thermo Fisher, 2023; Intertek, 2023).

Methods

Experimental preparation of samples

The term natural rubber refers to cis-1,4-polyisoprene, one of the most important natural polymers. It is obtained from the *Hevea Brasiliensis* (natural rubber), which grows in tropical areas of Middle and South America and Asia. Natural rubber is soft and sticky at higher temperatures and solid and brittle at lower temperatures. Thus, natural rubber is not suitable for direct usage. Therefore, it has to be subdued to the process of cross-linking; the result of this process is a useful form of rubber. In contrast to natural rubber, this rubber is not sticky or soft at higher temperatures or solid or brittle at lower temperatures. It is also highly elastic with a certain strength. The research was carried out on natural rubber samples to test the morphology of samples in the state of uniaxial deformation with the same radiation dose. The prepared latex was subjected to γ-radiation, during which ^{60}Co was used as the radiation source. Radiation was carried out in the Laboratory for Radiation Chemistry and Dositometry at the Institute Ruđer Bošković in Zagreb. The research used centrifuged latex of natural rubber that contains 60 % of dry matter, the manufacturer of which is the Rubber Research Institute of India. The amount of latex was measured so that films of 1 mm thickness were obtained.

Samples of natural rubber, treated in the way described above, were analyzed. A primary radiation dose of 200 kGy and a secondary radiation dose of 100 kGy, with a certain degree of deformation, were applied (Table 2).

Deformation degree is defined by the following expression:

Table 2. Varying of the secondary radiation dose and of the deformation degree

Primary dose / kGy	Secondary dose / kGy	Deformation degree
200	100	1.5
	100	2
	100	2.7

$$\varepsilon = \frac{l - l_0}{l_0} \quad (1)$$

where l is the length of the deformed sample and l_0 is the length of a sample in a relaxed state (Figure 1).

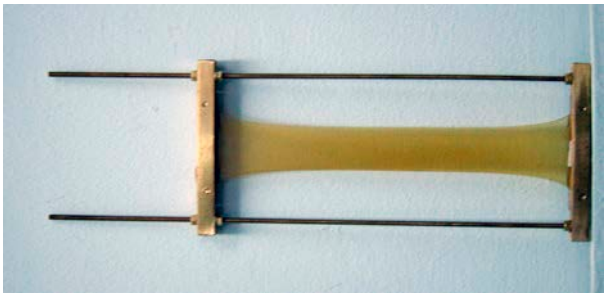


Figure 1. Deformation of natural rubber films before the secondary radiation dose

SEM analysis

A powerful technique in material analysis is scanning electron microscopy (SEM). Energy-dispersive X-ray spectrometry (EDX), in combination with SEM, provides an elemental analysis in areas of small nanometer diameters. The surface of the sample was scanned with a focused electron beam. Electron bombardment leads to the emission of secondary electrons, the backscattering of high-energy primary electrons, and the generation of element-specific X-rays. The impact of the electron beam on the sample produces X-rays that are characteristic of the elements present on the sample.

Measurement results

The samples were recorded with a scanning electronic microscope with an SEM Quanta 250 FEI emission field at the Metal Investigation Center Metris in Pula. The samples were recorded in conditions of a low vacuum, without steaming with gold, at an increase of 500× magnification (Figure 2).

The morphology of the samples' surface was recorded at the values of ε = 1.5, 2, and 2.7 and at an increase of 500× magnification (Figures 3, 4, and 5).

The effect of deformation was analyzed for the same total radiation dose, and the morphology of the sample surfaces, recorded with the microscope, was observed. It is perceived that the samples' surfaces are changed, with the same total dose applied, but by different amounts. The increase in deformation applied to samples affects the change in the number of pores visible at the surface of the sample as well

Figure 2. Scanning electron microscope (SEM) QUANTA 250 FEI Metris Center in Pula

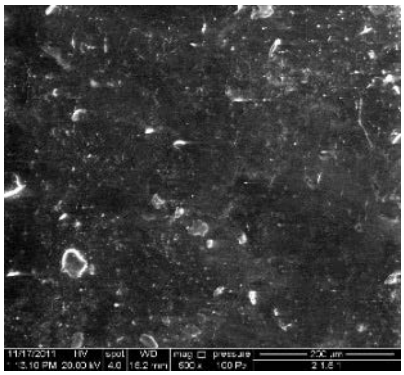


Figure 3. Sample 2-1.5-1 micrograph

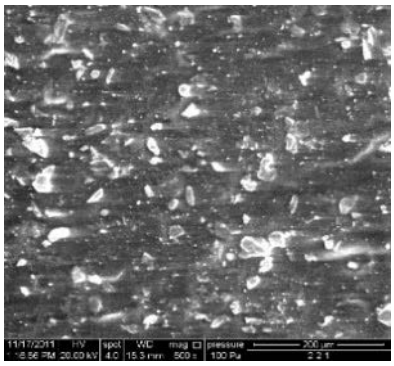


Figure 4. Sample 2-2-1 micrograph

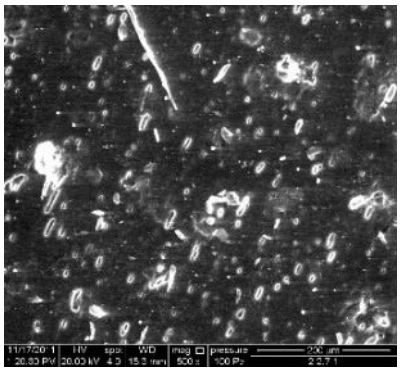


Figure 5. Sample 2-2.7-1 micrograph

as the change in their dimension. Therefore, in cases of lower deformation, the dimensions of the resulting pores are smaller. At the samples' surface, traces of impurities are observed as well.

For $\varepsilon = 2.7$, the position of the pore is visible at the surface of the sample in the direction of stretching. The formation of pores can occur prior to the formation of cracks. This is typical for amorphous polymers, and it can occur as a result of straining.

EDX analysis

An energy-dispersive X-ray analysis is a technique used by scientists in materials engineering. Under normal conditions, the positions of electrons within an atom belong to certain shells, which have different, discrete energies (Figure 6). An EDX analysis operates via a beam of electrons hitting the inner shell of an atom, knocking an electron out of the shell, and leaving behind a positively charged electron hole. When an electron is displaced, it attracts another electron from the outer shell to fill the vacancy. As the electron moves from the outer, higher-energy to the inner, lower-energy shell of the atom, the energy difference can be released in the form of an X-ray (depicted as a red dashed arrow in Figure 6). The energy of this X-ray is unique to a particular element and transition. Thus, researchers can quickly generate information about the chemical composition of the sample, including the elements that are present, as well as their distribution and concentration.

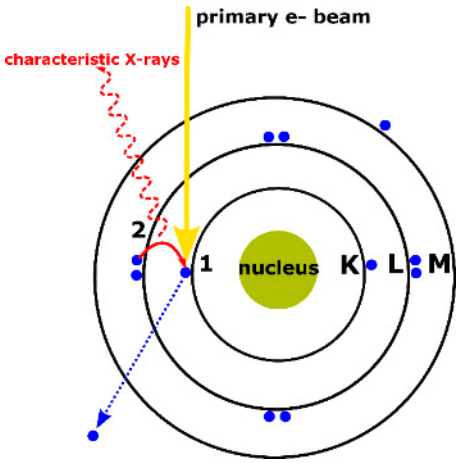
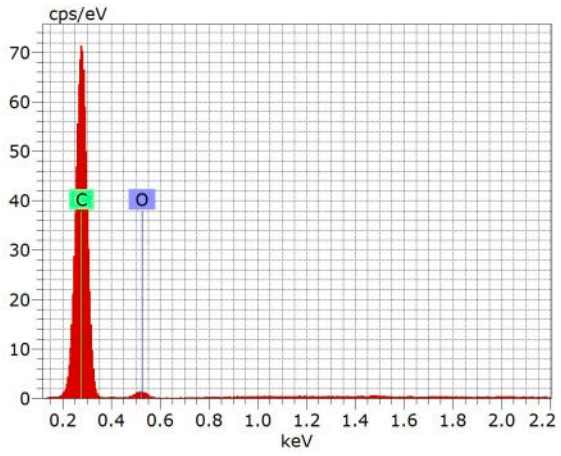


Figure 6. X-rays generated by electron beam interaction

Measurement results

EDX systems are connected to devices for electronic microscopy, i.e., SEM, which are used to examine air morphology. The data obtained through EDX analyses consist of spectra that add up to a microscopic map of the representation of individual elements of the sample analyzed. In this way, researchers can characterize their materials at the atomic level, and they can analyze various types of samples as well.

Figures 7, 9, and 11 show typical EDX spectra of the analyzed samples. The position of the peak leads to the identification of elements, and the height of the peak helps quantify the concentration of each element in a sample. The spectrum for the sample has a relatively high peak for carbon and a rather small peak for oxygen, whereas the spectrum for the difference is smaller.



El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
C	6	K-series	81.30	81.30	85.27	25.2
O	8	K-series	18.70	18.70	14.73	6.8
Total:			100.00	100.00	100.00	

Figure 7. EDX spectra (sample 2-1.5-1)

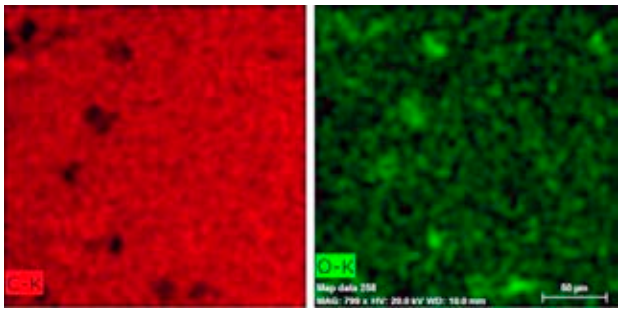
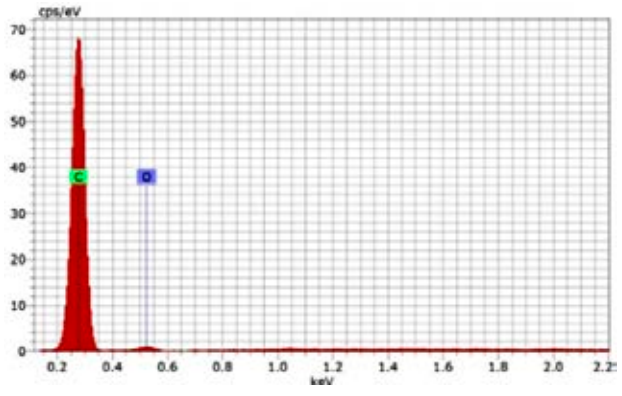


Figure 8. EDX sample 2-1.5-1 element map



El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
C	6	K-series	81.30	81.30	85.27	25.2
O	8	K-series	18.70	18.70	14.73	6.8
Total:			100.00	100.00	100.00	

Figure 9. EDX sample 2-2-1 spectrum

Morphological change is quantified by the structure of the pores at the sample's surface at a certain

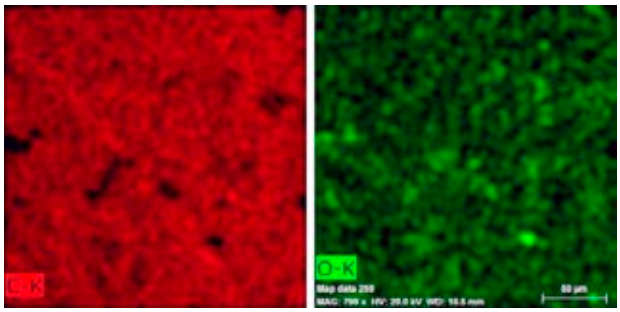
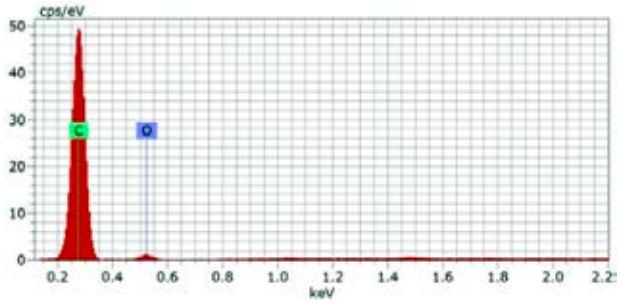


Figure 10. EDX elements map for the sample 2-2-1



El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
C	6	K-series	80.26	80.27	84.42	24.9
O	8	K-series	19.73	19.73	15.58	7.2
Total:			100.00	100.00	100.00	

Figure 11. EDX spectrum for sample 2-2.7-1

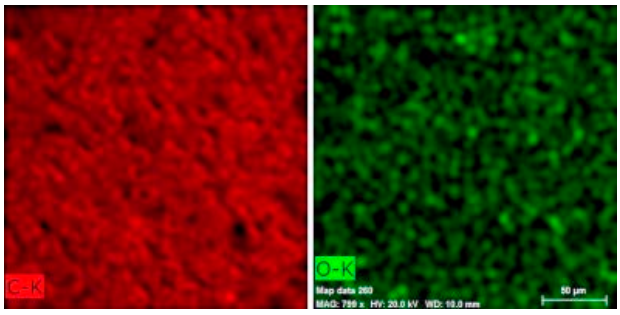


Figure 12. EDX elements map for the sample 2-2.7-1

total radiation dose, depending on the level of deformation (Figures 8, 10, and 12). Strains in elastomer materials depend on the level of cross-linking and the level of crystallinity (Trabelsi, Albouy & Rault, 2004). At deformations, i.e., $\varepsilon = 2.5$, the influence of the force usually leads to partial crystallinity of material and, therefore, to dynamic and orientation changes in the amorphous phase (Rault et al., 2006b).

Experimental results and analysis

The demands of growing reliability and safety, with the use of new technologies, impose the application

of new methods of analyses of the properties and the behavior of materials. Scanning electron microscopy (SEM) is one of the most suitable methods to characterize and analyze the morphology of a material. Characterization and identification of a material are based on determining characteristic materials or groups in a material. Hereby, the composition of other elements characterizes this material as different, and variations are easily recognizable. This is why the surfaces of the samples are scanned at the increase of 500× magnification, and the results of EDX analyses are presented in spectra. By processing these spectra, the EDX method provides data on the atoms present in a material, by color coding the layers and locations with information on the elemental composition of the samples (Figures 8, 10, and 12).

Conclusions

When they are exposed to γ-radiation, chemical processes occur in the polymers that result in various damages to the polymers, which affect their service life and useful properties. EDX, in combination with SEM, provides the possibility of analyzing different surface morphologies of natural rubber, as well as pore structures on the surface of the samples, due to the change in the degree of deformation for the same total dose of radiation.

It can be assumed that the processes followed by structural changes lead to the destruction of polymer material quality (for example, deterioration of their mechanical properties, a decrease of strength, change in color, etc.) and to total loss of functionality of a material. The influence of radiation is only one of the causes of these phenomena, and the process of degradation of elastomers is affected by other causes like temperature change or humidity. The influence of the marine environment on their durability indicates the need to find the influence of the important parameters for the sake of safety in the application of elastomer products in seamanship.

To fully define the application properties, it is essential to conduct the analyses of mechanical properties, such as strength, elongation at the breaking point, and elasticity module, in further research. The low elasticity module is the most important characteristic of elastomers, which enables their usage in numerous industry branches. Material testing enables product development according to expected specifications, which requires an understanding of the chemical structure of materials.

In future research, it is important to connect the matrix structure to the macroscopic properties of a material and to compare it with experimental and table values. This would enable the prediction of material behavior and their construction components, as well as an improved understanding and wider use of elastomer materials.

References

1. Billmeyer, F.W. (1984) *Textbook of Polymer Science*. 3rd Edition. New York: John Wiley & Sons.
2. Bokobza, L. (2005) Infrared analysis of elastomeric composites under uniaxial extension. *Macromolecular Symposia* 220 (1), pp. 45–60, doi: 10.1002/masy.200550204.
3. Čatić, I., Barić, G., Cvjetičanin, N., Galić, K., Godec, D., Grančarić, A.M., Katavić, I., Kovačić, T., Raos, P., Rogić, A., Rujnić-Sokele, M., Vranješ, N., Vrsaljko, D. & Andričić, B. (2010) Polymers – from the primeval beginning to plastics and elastomers. *Polimeri* 31 (2), pp. 59–70.
4. Esih, I. (2003) *Osnove površinske zaštite*. Zagreb: FSB.
5. Intertek (2023) *Energy Dispersive X-Ray Analysis* (*EDX*). [Online]. Available from: https://www.intertek.com/analysis/microscopy/edx/ [Accessed: April 15, 2024].
6. Janović, Z. (1997) *Polimerizacija i polimeri. HDKI – Kemija u industriji*. Zagreb.
7. Kendrick, L.H. & Caccese, V. (2005) *Development of a cavitation erosion resistant advanced material system*. Master Thesis, the University of Maine.
8. Miyamoto, Y., Yamao, H. & Sekimoto, K. (2003) Crystallization and melting of polyisoprene rubber under uniaxial deformation. *Macromolecules* 36 (17), pp. 6462–6471, doi: 10.1021/ma0342877.
9. Pintaric, A. (2009) *Inženjerski materijali u elektrotehnici*.
10. Rault, J., Marchal, J., Judeinstein, P. & Albouy, P.A. (2006a) Chain orientation in natural rubber, Part II: ^{2}H-NMR study. *The European Physical Journal E* 21 pp. 243–261, doi: 10.1140/epje/i2006-10064-6.
11. Rault, J., Marchal, J., Judeinstein, P. & Albouy, P.A. (2006b) Stress-induced crystallization and reinforcement in filled natural rubbers: ^{2}H-NMR study. *Macromolecules* 39 (24), pp. 8356–8368, doi: 10.1021/ma0608424.<
12. Roland, C.M. (2005) Structure characterization in the science and technology of elastomers. In: Mark, J.E., Erman, B., Eirich, F.R. (Eds) *The Science and Technology of Rubber* (Third Edition), pp. 105–155. Burlington: Elsevier, doi: 10.1016/B978-0-12-464786-2.X5000-7.
13. Roslim, R., Jefri, J., Manroshan Singh, J.S., Siti Noor Suzila, M.U.H. & Amir Hashim, Md.Y. (2015) Characterizing physical properties of peroxide vulcanized natural rubber latex films. *Advanced Materials Research* 1134, pp. 236–242, doi: 10.4028/www.scientific.net/AMR.1134.236.
14. Sellaro, R., Sarver, E. & Baxter, D. (2015) A standard characterization methodology for respirable coal mine dust using SEM-EDX. *Resources* 4 (4), pp. 939–957, doi: 10.3390/resources4040939.
15. Thermo Fisher (2023) *Polymer Research. Polymer research enabled by electron microscopy techniques*. [Online]. Available from: https://www.thermofisher.com/hr/en/home/materials-science/polymers-research.html [Accessed: April 15, 2024].

16. Toki, S., Sics, I., Ran, S.F., Liu, L.Z., Hsiao, B.S., Murakami, S., Senoo, K. & Kohjiya, S. (2002) New insights into structural development in natural rubber during uniaxial deformation by in situ synchrotron X-ray diffraction. *Macromolecules* 35 (17), pp. 6578–6584, doi: 10.1021/ma0205921.
17. Trabelsi, S., Albouy, P.A. & Rault, J. (2004) Stress-induced crystallization properties of natural and synthetic CIS-polyisoprene. *Rubber Chemistry and Technology* 77 (2), pp. 303–316, doi: 10.5254/1.3547825.
18. Valić, S., Andreis, M., Veksli, Z. & Charlesby, A. (1991) Matrix inhomogeneity in cross-linked rubber and rubber emulsions. *International Journal of Radiation Applications and Instrumentation. Part C. Radiation Physics and Chemistry* 37 (2), pp. 257–261, doi; 10.1016/1359-0197(91)90138-R.

Cite as: Bonato, J. (2024) Application properties and microscopic analysis of elastomer samples cross-linked by gamma radiation. S*cientific Journals of the Maritime University of Szczecin, Zeszyty Naukowe Politechniki Morskiej w Szczecinie* 78 (150), 15–21.