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A. JASKOT[1*], P. PALACZ[1]

ANALYSIS OF THE INFLUENCE OF ELEMENTAL ADMIXTURE CONTENT ON THE MECHANICAL PROPERTIES OF HYPERELASTIC MATERIALS

The results of the analysis of the influence of the content of elemental admixtures in hyperelastic materials on their mechanical properties were included in this paper. Rubber-based materials are often used in engineering practice. However, modelling these materials is a complex and time-consuming task. The aim of the research described in this paper was to demonstrate the relationship between the content of admixtures of elements from groups of hyperelastic materials of different hardness and tensile strength. The samples for testing were selected in a way that allowed testing of a wider group of incompressible materials. The tests proposed in the work included sample preparation and determination of the hardness of rubbers of selected groups. The first stage of the work included testing the chemical composition of selected rubber types in order to determine the concentration of admixtures. The next stage included conducting uniaxial tensile tests. The results of the comparative analysis were presented in a graphical and descriptive manner. The work showed that the level of element admixtures has an effect on the mechanical properties of hyperelastic materials.

Keywords: Hyperelastic materials; elemental admixture content; rubber-based materials; uniaxial tensile test

1. Introduction

Hyperelastic material research mainly involves studying the behaviour of a material under the influence of applied loads. The properties of hyperelastic materials are used to dampen or reduce vibrations or cushion the operation of machines. One of the characteristic properties of incompressible materials is the ability to achieve elongation several times their original shape and then return to it. For this reason, they are often very desirable fillers or complementary elements of mechanical systems and devices, where they are often subjected to dynamic impacts using the ability to reduce them. A proposal for the classification of groups of rubber-like materials using optical methods was proposed in [1]. The most general division of incompressible materials is into very hard, hard, medium hard, soft and foam rubbers [2].

In modelling hyperelastic material, the difficulty lies in using an appropriate material model, which depends on its mathematical description, or more precisely, on the constitutive relation that describes it. The first known generalized theoretical model describing the behaviour of rubber under compression and tension was the model formulated by Mooney [3]. Rivlin [4] developed a model that reduced the number of required input data, which resulted in a simplification of the problem. The description of the elastic behaviour of rubber-like materials in the range of large deformations was derived by Zahorski [5]. The Mooney-Rivlin model represents the strain energy density based on the principal strain invariants, while the Ogden model [6] represents the strain energy density based on the three principal stretches. The proposals for modelling hyperelastic materials using ANSYS are given in [7,8].

Rubber-like materials are created by vulcanizing natural or synthetic rubber, which is then further processed to obtain, among other things, the appropriate hardness. Fillers, plasticizers, activators, retarders, and other auxiliary substances are used in this process. Additives in the compositions of individual rubbers can affect the type and scope of application of hyperelastic materials. The analysis described in [9] carried out after rubber vulcanization, and tensile strength and heating tests showed that the strength of rubber composites increased with the increase in the share of carbon black. Adding anti-ageing substances provides protection of rubber against atmospheric factors or the adverse effects of ozone or oxygen. Antiozonants with waxes create a protective layer on the rubber surface, which protects it under static and dynamic stress conditions. Adding elements such as sulphur causes sulphur atoms to cross-link with rubber

[1] CZESTOCHOWA UNIVERSITY OF TECHNOLOGY, DEPARTMENT OF CIVIL ENGINEERING, FACULTY OF CIVIL ENGINEERING, 3 AKADEMICKA STR., 42-201 CZESTOCHOWA

* Corresponding author: anna.jaskot@pcz.pl

molecules, creating a network of chemical bonds, thanks to which it obtains better properties [10]. The higher the density of rubber cross-linking, the less elastic the rubber. Adding calcium carbonate to the mixture increases processability and improves the behaviour of the mass subjected to vulcanization and the results of permanent deformation after compression. The source of calcium in rubber can be primarily calcium carbonate ($CaCO_3$), which is a filler used to reduce the costs of rubber production. Increased calcium (Ca) content can affect the deterioration of mechanical properties of rubber, especially reducing elasticity, while increasing stiffness and brittleness. The use of silica affects the strengthening of rubber by acting as a reinforcing filler. It improves tear strength, modulus, and fatigue resistance. Aluminium hydroxide is a filler for resins that reduces the flammability of resins, shrinkage and thermal expansion, and increases mechanical strength. Zinc oxide is added to most rubber compounds, mainly to activate the action of organic rubber vulcanization accelerators [11]. Analysis of the structure and crystallization of natural rubber, which found that the temperature-induced crystallization rate was related to the average molecular weight of the crosslinks but not to the average molecular weight, was described in [12].

It is possible to reuse rubber by grinding it into granulates and dust and adding it to other materials or adding it to rubber mixtures [13,14]. In [15] studies were presented in which small pieces of rubber were used as an alternative to unmodified fine particles. It has been shown that the addition of granulate to the rubber mixture, regardless of its modification, causes a reduction in friction resistance and abrasive wear of its vulcanizates compared to vulcanizates without granulate. The authors of [16] attempted to characterize the hyperelastic properties of rubber based on the Ogden model, and based on the pattern search algorithm and the Levenberg-Marquardt algorithm. The proposed solution based on, as it was mentioned, a professional method that can realize a comprehensive adjustment of uniaxial stress, biaxial stress, was basis for obtaining an experimental data of plane stress and simple shear of hyperviscoelastic materials. In [17] the characterization of silicone samples and adaptation of well-known standard material models of finite hyperelasticity to experimental data are presented. The authors of [18] proposed a new method for precise estimation of nominal stress-strain relationships for rubbers under uniaxial tension, pure shear and equiaxial tension using a biaxial in-plane tensile tester. For small strains these states differ only slightly and correlations between them are not well defined for large deformations [19].

The scope of this article covers only rubber-like materials for industrial applications. Rubber materials for special purposes, e.g. for contact with food, were not tested. Three types of medium-hard rubber were tested in the work. NBR rubber (Nitril Butadiene Rubber) plates are resistant to, among others, the impact of greases, oils, petroleum products, mineral fats, while maintaining resistance to abrasion and mechanical damage. EPDM rubber (Ethylene Propylene Diene Monomer Rubber) sheets, thanks to their properties, are most often used in variable weather conditions (frost, heat), they are resistant to steam, ozone and UV radiation. On the other hand, SBR rubber (Styrene-Butadiene or Styrene-Butadiene) sheets are the most universal sheets used, among others, as soundproofing, vibration dampening and sealing elements.

In this work, the content of elemental admixtures was tested using a spectrometer for three groups of medium-hard rubbers, and tensile strength tests were performed. The sample testing process, its methodology and results are described in the following chapters of the work.

2. Specimens and experimental research

The tests were carried out on commonly used rubber plates from the medium-hard rubber groups with dimensions of 1000×1000 mm and thickness of 10 mm, which are made of three types of rubber mixtures: NBR, EPDM and SBR. In each tested group three samples were prepared for testing. The following subsections present the tests carried out in the scope of the content of elemental admixtures, hardness tests and uniaxial tensile tests. Three tests were carried out in each test. The preparation of samples and the test stands were also discussed. A list of the properties of the types of rubber used for testing, along with the technical parameters declared by the manufacturer, is presented in TABLE 1.

TABLE 1

List of tested rubber plates along with their technical parameters, as declared by the manufacturer

Parameter	**1.**	**2.**	**3.**
Type of rubber	NBR	EPDM	SBR
Name	UOD	CWE	SGS
Hardness [Sh A]	70	65	65
Density [g/cm^3]	1.45	1.30	1.52
Tensile strength [N/mm^2]	4	6	2
Extensibility [%]	100	200	150
Temperature range [°C]	–30 to 100	–40 to 120	–30 to 70

2.1. Chemical analysis

The tested material groups were subjected to analysis of the elemental composition of inorganic admixtures (within the measurement range of the XRF spectrometer), i.e. heavy metals (Pb, Cd, Hg, Cr, Ni, Zn, Fe), fillers (Si, Ca, Mg, Al), vulcanization activators (Zn) and impurities. Samples were taken from the analysed rubber plates in the form of dust with particle dimensions smaller than 1 mm, being waste resulting from milling. The samples taken are shown in Fig. 1.

Appropriately prepared samples (three for each type of rubber) were weighed and placed in an energy-dispersive X-ray fluorescence spectrometer (XRF) (Fig. 2).

Using the SPECTRO XEPOS D spectrometer it was possible to determine the elemental composition in the range from sodium (Na-11) to uranium (U-92) in the periodic table.

Fig. 1. Test samples in the form of dust: a) NBR rubber; b) EPDM rubber; c) SBR rubber

Fig. 2. Samples placed in the SPECTRO XEPOS spectrometer

2.2. Hardness analysis

The rubber hardness test was carried out using a Teclock Shore A GS-719R hardness tester (durometer) mounted on a Teclock GS-615 stand (Fig. 3).

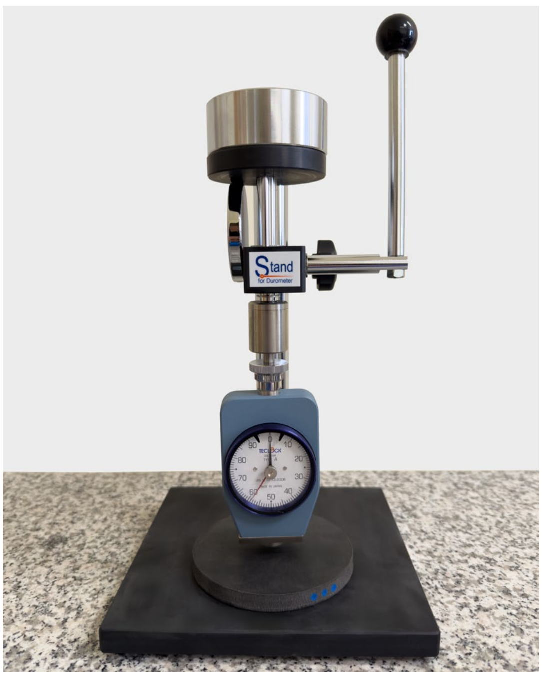

Fig. 3. Hardness tester Teclock Shore A

Each of the analysed rubber types was subjected to hardness tests. Samples in the form of 100 mm diameter discs were cut out from the tested rubber plates (three for each type). Before testing, the samples were conditioned for 24 hours at a temperature of 23 ± 2°C and humidity of 50 ± 5%. Measurements were taken in six locations on each of each discs, at least 10 mm from the edge of the sample.

2.3. Tensile strength analysis

In the next stage, the analysed rubbers were subjected to tensile tests. From the tested rubber plates, dumbbell-shaped samples were cut out in accordance with the standard [20], as shown in Fig. 4.

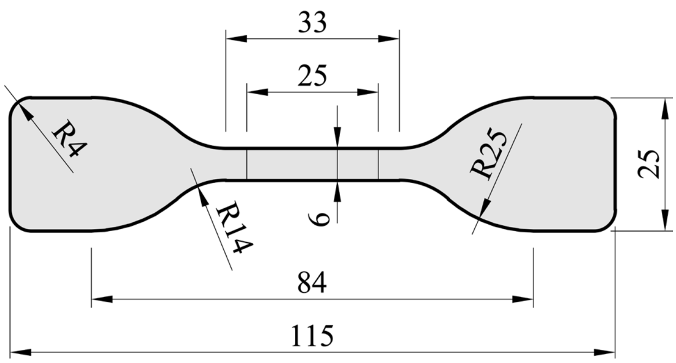

Fig. 4. Sample for testing strength in uniaxial tensile test, according to standard [20] type 1, [mm]

The samples were modelled according to their shape and their machining was programmed in the Autodesk Fusion 360 educational version. Then, samples were cut from the rubber plates using a CNC milling machine (three for each type of rubber), shown in Fig. 5. Due to the thickness of the analysed plates, the samples for analysis were left with a thickness of approx. 10 mm. Before the tensile test, the thickness and width of each sample were measured in three places at the narrowing point, then the samples were placed in the Shim-pol EZ Test EZ-LX 5 kN testing machine, each of the samples being clamped appropriately using clamps.

Fig. 5. Photo of the sample after cutting by machining using a CNC milling machine

Before starting the test, the testing machine was calibrated, then the samples were stretched at a speed of 100 mm/min until they broke. The view of the testing machine is shown in Fig. 6.

Fig. 6. Shim-pol EZ Test EZ-LX 5 kN testing machine

3. Results and discussion

As a result of the analysis of the elemental composition using a spectrometer, the content of individual elements in the tested samples was determined within the measurement range of the XRF spectrometer. The X-ray diffraction patterns measured for the tested samples have been shown in Fig. 7.

The average content of individual elements in the samples is presented in TABLE 2.

TABLE 2

Elemental composition of the tested rubbers
(taking into account admixtures)

Element	Average contents in samples by weight [%]		
	1. NBR	**2. EPDM**	**3. SBR**
Ca	26.73	19.88	20.45
Zn	4.60	2.34	0.79
S	4.53	4.47	2.16
Si	2.29	5.12	5.01
Al	0.91	4.20	4.66
Cl	0.71	0.04	0.04
Mg	0.51	0.30	0.52
Fe	0.07	0.26	0.21
K	0.04	0.38	0.11
Sr	0.01	0.03	0.03
Ti	0.01	0.16	0.13

Based on the analysis of the elemental composition of the tested samples (TABLE 2), it was shown that the dominant filler admixture in the tested samples is calcium (Ca) at the level of 26.73% in NBR rubber, 20.45% in SBR rubber and 19.88%

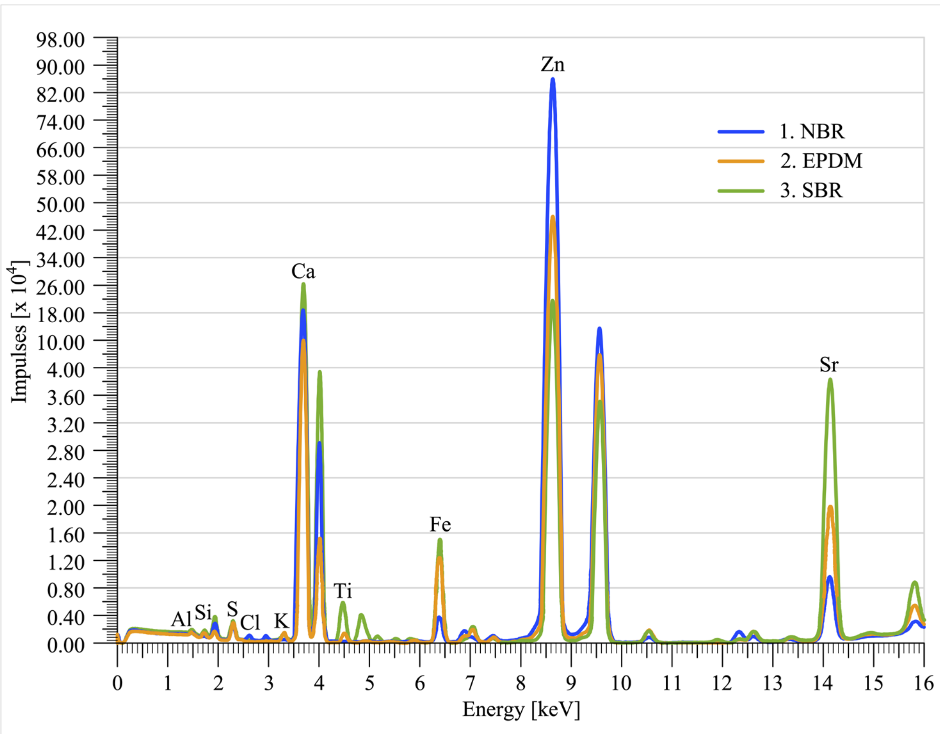

Fig. 7. X-ray diffraction (XRD) analysis for sample

in EPDM rubber. The second important component in NBR rubber is zinc (Zn) at 4.60%, while in EPDM and SBR rubber it was detected at 2.34% and 0.79%, respectively. The highest detected zinc (Zn) content in NBR rubber (4.60%) indicates high vulcanization activation, which improves chemical resistance, as confirmed by the material characteristics. The average zinc (Zn) content in EPDM rubber (2.34%) can be an additive to improve resistance to weather conditions (frost, heat) and to ozone and UV radiation, which is also confirmed by the material characteristics of the rubber. The low zinc (Zn) content in SBR rubber (0.79%) could mean that SBR rubber has lower mechanical, ageing and thermal resistance than NBR and EPDM rubber. The next element analysed is sulphur (S), the content of which in the tested rubbers was 4.53% for NBR rubber, 4.47% for EPDM rubber and 2.16% for SBR rubber. Sulphur (S) is a key component of the vulcanization process, which transforms rubber into flexible and durable rubber, and its amount has a direct impact on the mechanical and operational properties of rubber. Increased sulphur content in NBR and EPDM rubbers may indicate excessive cross-linking, which may be the reason for higher brittleness compared to SBR rubber. The silicon (Si) content in the tested samples is 2.29% in NBR rubber, 5.12% in EPDM rubber and 5.01% in SBR rubber, respectively. The lower silicon (Si) content in NBR rubber does not worsen its resistance to chemical agents (oils, fuels), but it does reduce resistance to abrasion and ageing. The average silicon (Si) content in EPDM and SBR rubbers may have an impact on better resistance to abrasion, weather conditions and UV compared to NBR rubber. In turn, the aluminium (Al) content is 0.91% in NBR rubber, 4.20% in EPDM rubber and 4.66% in SBR rubber, which indicates higher abrasion resistance in the case of EPDM and SBR rubbers compared to NBR rubber. The remaining elements (Cl, Mg, Fe, K, Sr and Ti) in the tested rubbers were detected in concentrations below 1%, which may indicate that they are admixtures in small amounts or trace residues from production. As a result of the hardness tests carried out using a hardness tester (durometer), the hardness of the tested samples was determined on the Shore A hardness scale. The results of the rubber hardness measurement are presented in TABLE 3.

TABLE 3

The results of hardness measurement of the analysed rubbers

	Sample		
	1. NBR	2. EPDM	3. SBR
Hardness Shore A [ShA]	71	73	62

The hardness of the tested materials can be compared. The hardest rubber is EPDM with an average hardness of 73 ShA, followed by slightly lower hardness NBR with an average hardness of 71 ShA. The least hard rubber is SBR with an average hardness of 62 ShA. By relating the hardness results to the previously tested chemical composition, one can see a significant effect of calcium (Ca), zinc (Zn) and sulphur (S) content in NBR and EPDM rubbers on hardness. The higher the zinc (Zn) and sulphur (S) content, the harder the rubber. Silicon (Si) and aluminium (Al) can increase hardness, but not to the same extent as zinc (Zn) and sulphur (S). The higher aluminium (Al) content in EPDM rubber relative to NBR resulted in higher hardness of EPDM rubber. SBR rubber has lower hardness mainly due to lower zinc (Zn) and sulphur (S) content, which results in weaker vulcanization and higher flexibility.

As a result of the tensile test carried out using a testing machine, the maximum force F at break was obtained in relation to the deformation L for the tested samples. The tensile strength σ was calculated from formula (1) by dividing the maximum force F at break of the samples by the cross-sectional area of the samples A,

$$\sigma = \frac{F}{A} \tag{1}$$

The elongation at break was calculated using formula (2), where L_0 is the initial length and L is the length at break:

$$\varepsilon = \frac{L - L_0}{L_0} \cdot 100\% \tag{2}$$

The results obtained from the tensile tests of the samples are presented in TABLE 4.

TABLE 4

Tensile strength and elongation at break of the tested samples

Parameters	Sample		
	1. NBR	2. EPDM	3. SBR
Average tensile strength σ [MPa]	4.55	4.73	2.52
Average elongation at break ε [%]	207.45	335.68	600.20

The stress-strain relationship for the highest tensile strength samples, where $\Delta L = L - L_0$, is plotted in Fig. 8.

Based on the obtained measurements, the tensile strength and elasticity of the tested rubbers were compared. The highest tensile strength of 4.73 MPa was characteristic of EPDM rubber. Slightly lower strength was demonstrated by NBR rubber of 4.55 MPa, and the lowest strength was demonstrated by SBR rubber with a strength of 2.52 MPa. In terms of the highest elongation at break, the most elastic rubber is SBR with an elongation of 600.20%, followed by EPDM rubber with an elongation of 335.68%, and the least elastic rubber is NBR with an elongation of 207.45%. Analysing the correlation of the obtained results, it can be seen that EPDM rubber combines high strength with moderate elongation, the rubber has good mechanical properties but is not excessively stretchable, which may be due to the presence of hard fillers, i.e. silicon (5.12%) and aluminium (4.20%) and high sulphur content (4.47%), which causes intensive vulcanization, making the rubber more durable but slightly less flexible. NBR rubber has high tensile strength but relatively low elongation, which may be due to the high content of calcium (26.73%) and zinc (4.60%), which make the rubber harder but less stretchable. In turn, SBR rubber is the most elastic rubber and the least durable, because it has a lower content of sulphur (2.16%) and zinc (0.79%) compared to EPDM and NBR rubber.

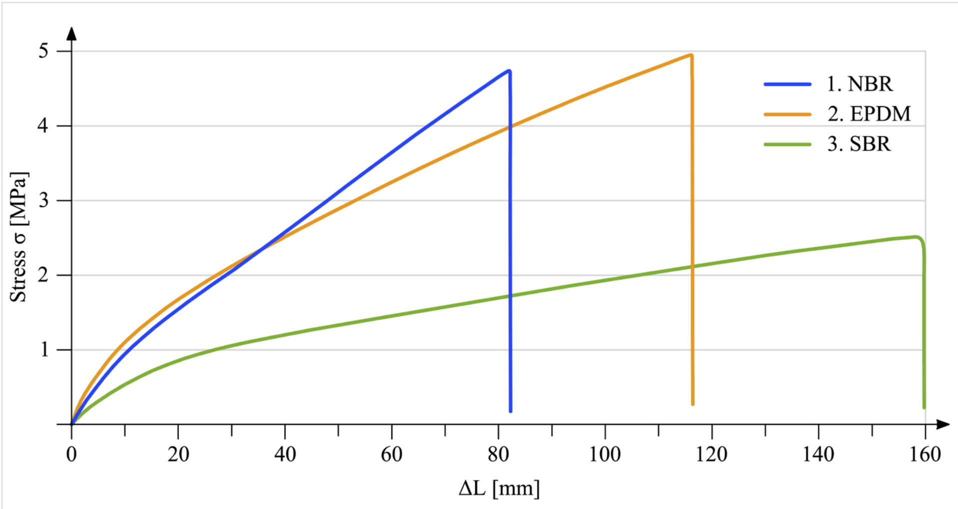

Fig. 8. Stress-strain relationship graph of the tested rubber samples

4. Conclusion

In this work, experimental studies of three types of hyperelastic materials from the group of medium-hard rubbers were conducted. The results obtained included the content of elemental admixtures, hardness tests and tensile strength tests in uniaxial tensile tests. Based on the conducted studies, the relationship resulting from the influence of compounds containing elements such as sulphur, silicon, calcium on the mechanical properties of the tested groups of rubber-like materials was confirmed. Higher sulphur content determined quantitatively in the work increases the strength of the material. Low sulphur content in the tested materials confirms their greater flexibility. High calcium content reduces flexibility, which makes the rubber harder. Further research will include quantitative studies to demonstrate the level of sulphur content and other significant admixtures on tensile strength. It is possible to determine mechanical properties based on the study of the elemental composition of the material. Small differences in the results result from the acceptance of the medium-hard rubber group for testing. Subsequent stages of research will also be carried out using soft and foam rubbers.

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