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INFLUENCE OF CROSSLINKING PARAMETERS ON THE QUALITY OF RUBBER PRODUCT

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Preliminary notes

The basis in the production of elastomeric materials is rubber which becomes cured during crosslinking process. Curing is a chemical-physical modification in which mostly plastic rubber transfers to rubber-elastic state. The curing process requires a curing agent, most frequently sulphur, and the process is performed at higher temperatures for several hours. The type of the used rubber defines the basic properties of product, for example: stability, ageing and flexibility at lower temperatures, as well as strength and elasticity. The paper presents the study of influence of crosslinking temperature and crosslinking time on some mechanical properties of natural rubber and styrene/butadiene rubber.

Key words: *crosslinking temperature, crosslinking time, mechanical properties, natural rubber, styrene/butadiene rubber*

Utjecaj parametara umreživanja na kvalitetu gumene tvorevine

Prethodno priopćenje

Osnova pri proizvodnji elastomernog materijala ili gume je kaučuk koji postaje umrežen tijekom procesa umreživanja. Umreživanje je kemijsko-fizikalna promjena pri kojoj pretežno plastični kaučuk prelazi u gumasto-elastično stanje. Za umreživanje je potrebno umreživalo, najčešće sumpor, a odvija se tijekom više sati pri povišenim temperaturama. Vrsta upotrebljenog kaučuka određuje temeljna svojstva gotovog gumenog proizvoda, prije svega postojanost, starenje, i savitljivost na niske temperature i dr., ali i mehanička svojstva, kao što su čvrstoća i elastičnost. U radu su primjenom centralno kompozitnog plana pokusa ispitana mehanička svojstva gumenih tvorevina od smjese prirodnog (NR) i stiren-butadienskog (SBR) kaučuka s obzirom na različite parametre umreživanja (vrijeme i temperatura umreživanja).

Ključne riječi: *mehanička svojstva, prirodni kaučuk, stiren-butadienski kaučuk, temperatura umreživanja, vrijeme umreživanja*

1 Introduction
Uvod

Rubber is a material without which one could not imagine today's world. The basic element for the production of rubber is caoutchouc which can be natural or synthetic. Natural rubber is extracted by tapping into the tropical rubber-tree (*lat. hevea braziliensis*) and by collecting the milky liquid -**latex**, which flows from the cut. Before crosslinking, rubber is mixed with additions according to precisely determined prescriptions, which ensures certain properties of the final product. Before crosslinking, rubber is in the form of tough mass, softeners are in the liquefied state, and other additions are powdery. [1] The task of rubber is to combine all the elements together and to determine for the rubber material the basic mechanical properties such as elasticity and strength. By combination with other additions other properties are determined as well (stability at higher or lower temperatures, toughness, oil resistance etc.).

2 Properties of materials
Svojstva materijala

Rubber materials based on NR rubber are resistant to the influence of water, alcohol, glycol, silicone oils and grease, and are not resistant to the influence of mineral oils and grease, aliphatic and aromatic as well as chlorinated hydrocarbons. They feature high elasticity, good impact resistance, slight permanent deformation under the action of load, good stability at low and high temperatures, wear resistance, and resistance to atmospheric influences [1, 2].

In case of SBR rubber the elasticity and permanent deformation under the action of load are lower than in case of natural rubber, whereas the resistance to atmospheric influences, heat stability and stability to alcohol-based oils (ATE oil) are higher. It retains good mechanical properties at low and high temperatures and has good stability to organic and inorganic acids as well as in water. It swells a lot in mineral oils and greases, petrol, aromatic, aliphatic and chlorinated hydrocarbons, and oils and grease of vegetable and animal origin. The remaining properties are very similar to the properties of natural rubber [2].

3 Eksperimental part
Eksperimentalni dio

In the experimental part, the central composite test plan was used to analyze the influence of the crosslinking time and the crosslinking temperature on the tensile strength, elongation at break, and hardness of the compound of natural and styrene/butadiene rubber.

3.1 Testing materials and equipment
Ispitni materijali i oprema

In the experiment a compound of rubber of factory designation *R – 122/5B*, based on NR/SBR (50:50) which denotes natural and styrene/butadiene rubber was used.

Empirical data indicate that for the crosslinking of the NR/SBR compound the heating plates are heated to a temperature of 165 °C. Apart from the crosslinking temperature the very important datum during compound crosslinking is also the time. However, when the crosslinking agent is sulphur, the data differ and the crosslinking time is taken empirically.

The compound crosslinking has been carried out on the press manufactured by *Machinenfabriek*, of maximal pressure of 35 t. Hardness was tested by a manual device for hardness testing according to Shore A, and mechanical properties were determined by using the tester *Messphysik Beta 50 – 5*, of maximal loading force of 50 kN (Fig. 1).

Figure 1 *Tensile testing machine*
Slika 1. *Kidalica*

3.2 Shape of the test specimen for determination of mechanical properties [3]
Oblik ispitnog tijela za određivanje mehaničkih svojstava

The shape of the test specimen (Fig. 2) for testing tensile strength R_m and elongation at break ε_p was determined according to ISO 37:1994 standard.

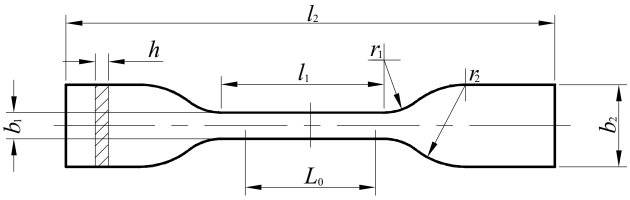

Figure 2 *Shape of test specimen*
Slika 2. *Oblik ispitnog tijela*

Tab. 1 shows the data about the dimensions of the test specimen.

Table 1 *Dimensions of test specimen*
Tablica 1. *Dimenzije ispitnog tijela*

	Dimension /mm
l_2 - overall length	75
b_2 - width of ends	12,5 ± 1,0
l_1 - length of narrow portion	25,0 ± 1,0
L_0 - gauge length	20,0 ± 0,5
b_1 - width of narrow portion	4,0 ± 0,1
h - thickness	2,0 ± 0,2
r_1 - transition radius outside	8,0 ± 0,5
r_2 - transition radius inside	12,5 ± 1,0

The tester is used to read the maximal force, and the tensile strength is calculated according to equation:

$$R_m = \frac{F_{max}}{A_0}, \tag{1}$$

where:
R_m – tensile strength, N/mm^2
F_{max} – maximal force, N
A_0 – initial area of the transversal cross-section, mm^2

Elongation at break is calculated according to equation:

$$\varepsilon = \frac{l_p - l_0}{l_0} \cdot 100, \tag{2}$$

where:
l_0 – initial specimen length, mm
l_p – test length at break of the specimen, mm.

Mechanical properties are determined on three specimens, as required by the standard, and the test temperature is 21 °C.

3.3 Central composite design
Centralno kompozitni plan pokusa

The central-composite test belongs to the group of higher order tests, so-called response surface methodology. The response surface methodology comprises a group of statistical and mathematical methods that are used to develop, improve and optimize the process. The measurable value of the product quality is called response. The knowledge about the response surface with sufficient precision, accuracy and reliability allows forecasting of the future results within the field of analyzed factors, and gives insight into the entire process [4].

The purpose of central-composite test is to generate a mathematical model, i.e. equations which describe the process. If the studied factors in the test are really those that affect the process, and the data obtained by test are of acceptable accuracy and precision, then it is possible to develop a model which credibly describes the process [4].

The values of crosslinking temperature and crosslinking time used for the main test – central-composite test with two factors – have been empirically defined. The values of the crosslinking temperature range from 151 °C to 179 °C, whereas the crosslinking time is in the range from 3,4 min to 7,6 min. Using a computer and *DesignExpert* software thirteen test states for both compounds were generated (Tab. 2).

***Table** 2 Levels of factors for NR/SBR*
Tablica 2. *Faktori i njihove razine za NR/SBR smjesu*

Levels	x_1 crosslinking temperature ϑ_u/ °C	x_2 crosslinking time t_u/ min
- 1,414	151	3,4
-1	155	4
0	165	5,5
+1	175	7
+1,414	179	7,6

3.4 Curing of compound
Umreživanje smjese

After having chosen the test plan the crosslinking of the rubber compound started to be carried out. First, pieces are cut from the compound, which are then placed into the mould. The mould is then heated to the required temperature together with the press heating plates, and the rubber compound is coated by a foil (in order to avoid adhesion of the rubber compound to the mould walls) and placed into the mould (Fig. 3). The mould is then inserted into the press. The mould with the rubber compound is kept in the press for a certain time under certain pressure according to the central-composite test plan.

Figure 3 *Rubber compound in the mould*
Slika 3. *Kaučukova smjesa uložena u kalup*

After having crosslinked the rubber compound in the press, the press is opened and demoulding is carried out. After demoulding the foil and flash are removed.

Table 3 *Parameters and calculated mean values of mechanical properties*
Tablica 3. *Parametri i izračunate srednje vrijednosti mehaničkih svojstava*

Run	Crosslinking temperature ϑ_u/ °C	Crosslinking time t_u/ min	Tensile strength R_m/ N/mm^2	Strain ε_p/ %	Hardness H/ Sh A
1	179	5,5	10,69	531,80	57,67
2	165	5,5	15,02	702,37	58,22
3	155	4	9,78	687,17	53,33
4	175	7	11,51	475,93	59,44
5	175	4	12,24	507,73	60,11
6	165	3,4	13,85	639,07	56,78
7	165	7,6	14,51	566,70	60,11
8	165	5,5	15,04	593,73	60,11
9	155	7	13,58	671,57	55,89
10	165	5,5	14,31	549,70	60,22
11	151	5,5	10,56	644,03	55,22
12	165	5,5	14,85	612,47	59,78
13	165	5,5	13,82	582,40	60,00

3.5 Results of mehanical properties of NR/SBR
Rezultati ispitivanja mehaničkih svojstava kaučukove smjese NR/SBR

Tab. 3 shows the parameters and mean values of the measured mechanical properties.

Fig. 4 shows the diagram of the tensile stress and elongation of all the 13 test states for the NR/SBR compound.

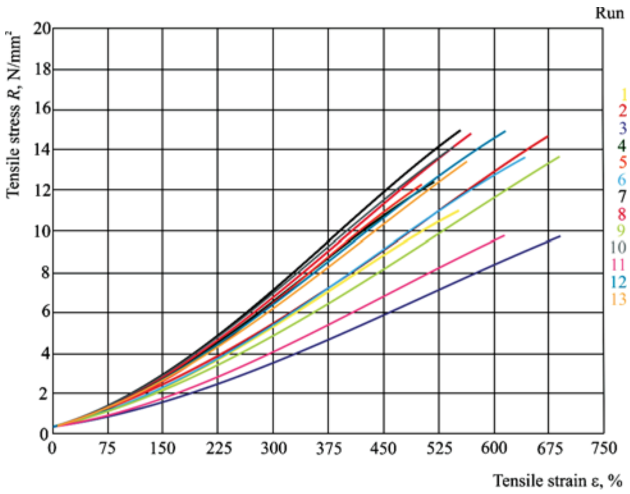

Figure 4 *Diagram of tensile stress – elongation for the NR/SBR compound*
Slika 4. *Dijagram rastezno naprezanje – istezanje za smjesu NR/SBR*

3.5.1 Influence of crosslinking temperature and time on tensile strength for NR/SBR
Utjecaj temperature i vremena umreživanja na rasteznu čvrstoću NR/SBR

For the NR/SBR compound, for each of the 13 states of crosslinking temperature and time three specimens were made which were subjected to the tensile strength test. The data have been processed by the *DesignExpert* software – ANOVA (variance analysis) module, which is presented in Tab. 4.

Table 4 *Analysis of variance – tensile strength for NR/SBR*
Tablica 4. *Rezultati analize varijance – rastezna čvrstoća za NR/SBR*

		Sum of squares	Degrees of freedom	Mean square	F value	Risk of rejection of H_0
Model		39,32	5	7,86	22,18	0,0004
	x_1	0,041	1	0,041	0,12	0,7433
	x_2	2,00	1	2,00	5,65	0,0491
	x_1^2	32,09	1	32,09	90,51	< 0,0001
	x_2^2	0,95	1	0,95	2,69	0,1450
	x_1x_2	5,13	1	5,13	14,47	0,0067
Residual		2,48	7	0,35		
	Lack of fit	1,36	3	0,45	1,61	0,3207
	Pure error	1,12	4	0,28		
Cor Total		41,80	12			

Tab. 4 shows that the factors x_2, x_1^2, x_1x_2 are significant. Fig. 5 shows the dependence of tensile strength on the crosslinking temperature and time.

The presentation of the dependence of tensile strength of the crosslinked NR/SBR compound on crosslinking temperature and time shows that the networking time affects the increase in the value of tensile strength, and the tensile strength has maximal value at the mould wall temperature of about 165 °C. Based on the carried out analysis of the experiment results one may conclude that the optimal crosslinking area of this compound is the range of temperatures from 160 °C to 170 °C.

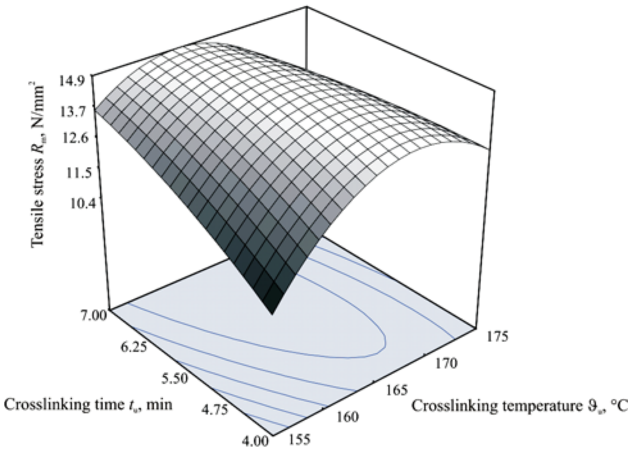

Figure 5 *The dependence of tensile strength on the crosslinking time and temperature for NR/SBR*
Slika 5. *Prikaz ovisnosti rastezne čvrstoće o vremenu umreživanja i temperaturi umreživanja za smjesu NR/SBR*

An overview of the statistical data about the model is presented in Tab. 5. The determination coefficient is a deviation measure from the arithmetic mean which has been explained by the model. The closer the value of the determination coefficient to one, the better the model follows the data.

Table 5 *Summary statistics for the model*
Tablica 5. *Statistički podaci modela*

Standard deviation	0,60
Mean	13,06
Coefficient of determination	0,9406

The model for tensile strength can be described by the following equation (values x_1 and x_2 are entered in a coded form):

$$R_m = 14{,}61 + 0{,}072 \cdot x_1 + 0{,}50 \cdot x_2 - 2{,}15 \cdot x_1^2 - \\ - 0{,}37 \cdot x_2^2 - 1{,}13 \cdot x_1 \cdot x_2 . \quad (3)$$

So that e.g. for x_1 = 170 °C (the coded value = 0,5) and x_2 = 3 min (the coded value = – 0,2) the expected tensile strength will amount to R_m = 14,1 N/mm².

3.5.2 Influence of crosslinking temperature and time on elongation at break for NR/SBR
Utjecaj temperature i vremena umrežiavanja na prekidno istezanje NR/SBR

The next test for the NR/SBR compound that was carried out on the test specimens is elongation at break. The results of the variance analysis are presented in Tab. 6.

Table 6 *Analysis of variance – elongation at break for NR/SBR*
Tablica 6. *Rezultati analize varijance – prekidno istezanje za NR/SBR*

		Sum of squares	Degrees of freedom	Mean square	F value	Risk of rejection of H_0
Model		38420,44	2	19210,22	9,21	0,0054
	x_1	35617,43	1	35617,43	17,08	0,0020
	x_2	2803,01	1	2803,01	1,34	0,2732
Residual		20851,06	10	2085,11		
	Lack of fit	7667,58	6	1277,93	0,39	0,8560
	Pure error	13183,47	4	3295,87		
Cor Total		59271,49	12			

In this case factor x_1 is significant. Fig. 6 shows the dependence of elongation at break on the crosslinking temperature and time.

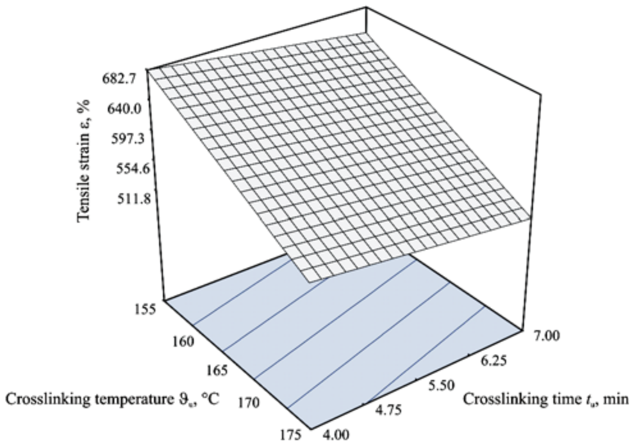

Figure 6 *The dependence of elongation at break on the crosslinking time and temperature for NR/SBR*
Slika 6. *Prikaz ovisnosti prekidnog istezanja o vremenu umrežiavanja i temperaturi umrežiavanja za smjesu NR/SBR*

As can be seen from Fig. 6 the value of extension by raising the temperature and time declines. This decline of the extension value is completely logical since the compound loses its extension ability over longer time and higher temperature of crosslinking.

The overview of statistical data about the model is presented in Tab. 7.

Table 7 *Summary statistics for the model*
Tablica 7. *Statistički podaci modela*

Standard deviation	45,66
Mean	597,28
Coefficient of determination	0,6482

The model for elongation variable can be described by the equation (values x_1 and x_2 are entered in the coded form):

$$\varepsilon = 597{,}28 - 66{,}72 \cdot x_1 - 18{,}72 \cdot x_2 . \quad (4)$$

So that e.g. for x_1 = 170 °C (the coded value = 0,5) and x_2 = 3 min (the coded value = – 0,2) the expected elongation will be ε = 567,7 %.

3.5.3 Influence of crosslinking temperature and time on hardness for NR/SBR
Utjecaj temperature i vremena umreživanja na tvrdoću NR/SBR

Hardness testing was measured on three points on all the three test specimens, and the total mean value was calculated. The hardness variance analysis is presented in Tab. 8.

Table 8 *Analysis of variance – hardness for NR/SBR*
Tablica 8. *Rezultati analize varijance – tvrdoća za NR/SBR*

		Sum of squares	Degrees of freedom	Mean square	F value	Risk of rejection of H_0
Model		53,00	5	10,60	7,74	0,0090
	x_1	23,93	1	23,93	17,48	0,0041
	x_2	5,39	1	5,39	3,94	0,0876
	x_1^2	19,49	1	19,49	14,24	0,0070
	x_2^2	3,16	1	3,16	2,31	0,1726
	x_1x_2	2,72	1	2,72	1,99	0,2013
Residual		9,58	7	1,37		
	Lack of fit	6,83	3	2,28	3,31	0,1390
	Pure error	2,75	4	0,69		
Cor Total		62,58	12			

In this case factors x_1, x_1^2 are significant. Fig. 7 shows the dependence of hardness on the crosslinking temperature and time.

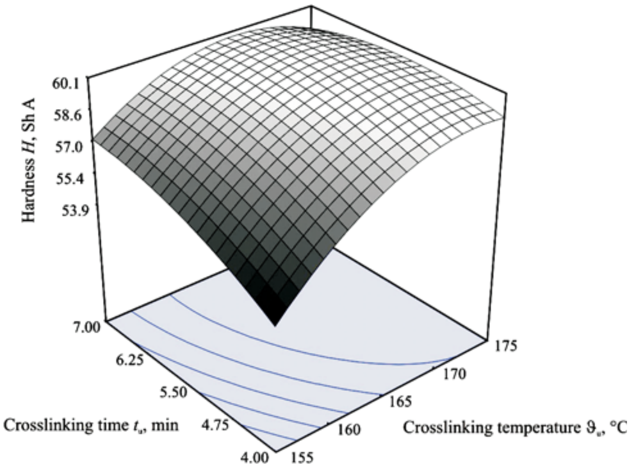

Figure 7 *The dependence of hardness on the crosslinking time and temperature for NR/SBR*
Slika 7. *Prikaz ovisnosti tvrdoće o vremenu umreživanja i temperaturi umreživanja za smjesu NR/SBR*

As can be seen from the presentation of the dependence of hardness on time and temperature of crosslinking the temperature factor has positive influence on the increase in the value of hardness at temperatures of 155 °C to 170 °C, whereas it increases slightly after this temperature

The overview of statistical data about the model is presented in Tab. 9.

Table 9 *Summary statistics for the model*
Tablica 9. *Statistički podaci modela*

Standard deviation	1,17
Mean	58,22
Coefficient of determination	0,8469

The model for the hardness variable can be described by the following equation (values x_1 and x_2 are entered in the coded form):

$$H = 59{,}66 + 1{,}73 \cdot x_1 + 0{,}82 \cdot x_2 - 1{,}67 \cdot x_1^2 - - 0{,}67 \cdot x_2^2 - 0{,}82 \cdot x_1 \cdot x_2 \,. \quad (5)$$

So that e.g. for x_1 = 170 °C (the coded value = 0,5) and x_2 = 3 min (the coded value = – 0,2) the expected hardness amounts to H = 59,86 Sh A.

4 Conclusion
Zaključak

In the experimental part of the work the tensile strength, elongation at break and hardness for the rubber compound of natural and styrene/butadiene (NR/SBR) were measured. The obtained results were processed by means of the *DesignExpert* software package which generated the models which show the influence of the crosslinking temperature and time on these mechanical properties.

The research has shown that in case of NR/SBR compound the crosslinking temperature affects most the ultimate stress and hardness, and the crosslinking time affects the tensile strength. In case of this compound the data about crosslinking time and temperature obtained from practice proved to be accurate, which shows that there are not many possibilities to optimize the production conditions.

Individual results have also been affected by the non-homogeneous structure, i.e. residual air bubbles.

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5 References
Literatura

[1] Šercer, M. Proizvodnja gumenih tvorevina. // Društvo za plastiku i gumu : Zagreb, 1999.
[2] N. N. Gumeni materijali – svojstva i primjena, http://bek.hr/Files/materijali%20izrade.doc, 03.03.2008.
[3] ISO 37:1994 Rubber, vulcanized or thermoplastic – Determination of tensile stress – strain properties
[4] Rujnić-Sokele, M. Optimiranje procesa proizvodnje puhanih proizvoda od poli(etilen - teraftalata), magistarski rad, Fakultet strojarstva i brodogradnje, Zagreb, 2002.

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