INFLUENCE OF CROSSLINING PARAMETERS ON THE QUALITY OF RUBBER PRODUCT

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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

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
Ekspertimentalni 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]

**Table 1 Dimensions of test specimen**

| Dimension /mm | 
|----------------|------------------|------------------|
| $l_2$ - overall length | 75 | 
| $b_2$ - width of ends | $12.5 \pm 1.0$ | 
| $l_1$ - length of narrow portion | $25.0 \pm 1.0$ | 
| $L_0$ - gauge length | $20.0 \pm 0.5$ | 
| $b_1$ - width of narrow portion | $4.0 \pm 0.1$ | 
| $h$ - thickness | $2.0 \pm 0.2$ | 
| $r_1$ - transition radius outside | $8.0 \pm 0.5$ | 
| $r_2$ - transition radius inside | $12.5 \pm 1.0$ | 

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

![Figure 2 Shape of test specimen](Slika 2. Oblik ispitnog tijela)

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

$$ R_m = \frac{F_{\text{max}}}{A_0} $$  \hspace{1cm} (1)

where:

- $R_m$ – tensile strength, N/mm²
- $F_{\text{max}}$ – maximal force, N
- $A_0$ – initial area of the transversal cross-section, mm²

Elongation at break is calculated according to equation:

$$ \varepsilon = \frac{l_p - l_0}{l_0} \cdot 100, $$  \hspace{1cm} (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>
<thead>
<tr>
<th>Levels</th>
<th>$x_1$ - crosslinking temperature $\delta_1 / ^\circ C$</th>
<th>$x_2$ - crosslinking time $t_2 / \text{min}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1,414</td>
<td>151</td>
<td>3.4</td>
</tr>
<tr>
<td>-1</td>
<td>155</td>
<td>4</td>
</tr>
<tr>
<td>0</td>
<td>165</td>
<td>5.5</td>
</tr>
<tr>
<td>+1</td>
<td>175</td>
<td>7</td>
</tr>
<tr>
<td>+1.414</td>
<td>179</td>
<td>7.6</td>
</tr>
</tbody>
</table>

**Table 2 Levels of factors for NR/SBR**

**Tablelica 2. Faktori i njihove razine za NR/SBR smjesu**
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.

3.5 Results of mechanical 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 3 Rubber compound in the mould](image)

**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 rubber compound and the flash are removed.

**Table 3** Parameters and calculated mean values of mechanical properties

<table>
<thead>
<tr>
<th>Run</th>
<th>Crosslinking temperature $\theta_c$/°C</th>
<th>Crosslinking time $t_c$/min</th>
<th>Tensile strength $R_m$/N/mm²</th>
<th>Strain $e_p$/%</th>
<th>Hardness $H$/Sh A</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>179</td>
<td>5.5</td>
<td>10.69</td>
<td>531.80</td>
<td>57.67</td>
</tr>
<tr>
<td>2</td>
<td>165</td>
<td>5.5</td>
<td>15.02</td>
<td>702.37</td>
<td>58.22</td>
</tr>
<tr>
<td>3</td>
<td>155</td>
<td>4</td>
<td>9.78</td>
<td>687.17</td>
<td>53.33</td>
</tr>
<tr>
<td>4</td>
<td>175</td>
<td>7</td>
<td>11.51</td>
<td>475.93</td>
<td>59.44</td>
</tr>
<tr>
<td>5</td>
<td>175</td>
<td>4</td>
<td>12.24</td>
<td>507.73</td>
<td>60.11</td>
</tr>
<tr>
<td>6</td>
<td>165</td>
<td>3.4</td>
<td>13.85</td>
<td>639.07</td>
<td>56.78</td>
</tr>
<tr>
<td>7</td>
<td>165</td>
<td>7.6</td>
<td>14.51</td>
<td>566.70</td>
<td>60.11</td>
</tr>
<tr>
<td>8</td>
<td>165</td>
<td>5.5</td>
<td>15.04</td>
<td>593.73</td>
<td>60.11</td>
</tr>
<tr>
<td>9</td>
<td>155</td>
<td>7</td>
<td>13.58</td>
<td>671.57</td>
<td>55.89</td>
</tr>
<tr>
<td>10</td>
<td>165</td>
<td>5.5</td>
<td>14.51</td>
<td>549.70</td>
<td>60.22</td>
</tr>
<tr>
<td>11</td>
<td>151</td>
<td>5.5</td>
<td>10.56</td>
<td>644.03</td>
<td>55.22</td>
</tr>
<tr>
<td>12</td>
<td>165</td>
<td>5.5</td>
<td>14.85</td>
<td>612.49</td>
<td>59.78</td>
</tr>
<tr>
<td>13</td>
<td>165</td>
<td>5.5</td>
<td>13.82</td>
<td>582.40</td>
<td>60.00</td>
</tr>
</tbody>
</table>

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

**Table 4** Analysis of variance – tensile strength for NR/SBR

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>Sum of squares</th>
<th>Degrees of freedom</th>
<th>Mean square</th>
<th>F value</th>
<th>Risk of rejection of $H_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>39.32</td>
<td>5</td>
<td>7.86</td>
<td>22.18</td>
<td>0.0004</td>
</tr>
<tr>
<td>$x_1$</td>
<td>0.041</td>
<td>1</td>
<td>0.041</td>
<td>0.12</td>
<td>0.7433</td>
</tr>
<tr>
<td>$x_1^2$</td>
<td>2.00</td>
<td>1</td>
<td>2.00</td>
<td>5.65</td>
<td>0.0491</td>
</tr>
<tr>
<td>$x_2$</td>
<td>32.09</td>
<td>1</td>
<td>32.09</td>
<td>90.51</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>$x_2^2$</td>
<td>0.95</td>
<td>1</td>
<td>0.95</td>
<td>2.69</td>
<td>0.1450</td>
</tr>
<tr>
<td>$x_1x_2$</td>
<td>5.13</td>
<td>1</td>
<td>5.13</td>
<td>14.47</td>
<td>0.0067</td>
</tr>
<tr>
<td>Residual</td>
<td>2.48</td>
<td>7</td>
<td>0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack of fit</td>
<td>1.36</td>
<td>3</td>
<td>0.45</td>
<td>1.61</td>
<td>0.3207</td>
</tr>
<tr>
<td>Pure error</td>
<td>1.12</td>
<td>4</td>
<td>0.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>41.80</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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.

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.

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 umrežavanja 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.

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.
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.

In this case factors \( x_1 \) and \( x_2 \) are significant. Fig. 7 shows the dependence of hardness on the crosslinking temperature and time.

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.

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):

\[
H = 59.66 + 1.73 \cdot x_1 + 0.82 \cdot x_2 - 1.67 \cdot x_1^2 - 0.67 \cdot x_2^2 - 0.82 \cdot x_1 \cdot x_2.
\]  

(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 \( H = 59.86 \) ShA.

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 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.

Acknowledgement
Zahvala

This work is part of the research included in the project Increasing Efficiency in Polymeric Products and Processing Development, which is part of program Rapid Production — From Vision to Reality and project Experimental simulation of damages in mechanical and biomechanical structures, which is part of program Mechanical Structures and Biomaterials-Computer Simulations and Experiment supported by the Ministry of Science, Education and Sports of the Republic of Croatia. The authors would like to thank the Ministry for the financing of this project.

5 References
Literatura

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