Properties of Natural and Styrene-Butadiene Rubbers with Butadiene Rubber Blends I

Introduction
Since development of new synthetic polymers is very expensive, the standard polymers are often combined in order to obtain new materials with a broader spectrum of properties. Rubbers are mixed for many years, both from processing reasons, and because of requirements for the properties of the resulting rubber goods. It is very important to choose carefully blended rubbers and additives. Dissimilar immiscible rubbers can result in blends with inferior properties. This property failure has been ascribed to three types of incompatibility – thermodynamic, different viscosity and cure rate incompatibility [1].

A number of studies deals with the influence of blend composition on the distribution of fillers or the components of the curing system [2-5] and final properties of vulcanizates [6-9] including their morphology [10]. However, they don’t give any information about influence of mixing conditions or about behavior of rubbers.

This work is focused on the blends of natural and styrene-butadiene rubbers with butadiene rubber, which are widely used. The blends contain rubbers only because of elimination of potential side effect of the additives.

Experimental
Materials
The used elastomers were natural rubber (NR) LAC 10 (110 1+4 ML) from Liberia, styrene-butadiene rubber (SBR) Kralex 1500 (48 ML (1+4) 100 °C) with 24 wt % styrene content and butadiene rubber (BR) Synteca BR 44 (50 ML (1+4) 100 °C) both from Synthos Kralupy a.s., Czech Republic.

Blend preparation
BR, NR, SBR and their blends were processed on a laboratory two roll mill (roll diameter – 150 mm, length – 400 mm, friction ratio - 11:9, speed regulation – frequency inverter Danfoss, manufacturer - Bafa) and on internal mixer (Plasti-Corder lab-station, manufacturer - Brabender). Formulation of blends is in Tables 1 and 2.

The first sets of NR/BR and SBR/BR blends were prepared on a laboratory two roll mill. The mixing time was five minutes. The two roll mill was cooled by water. Blends were cut back and forth throughout. Speed of the slow roll was 18 rpm for NR/BR blends and 13 rpm for SBR/BR blends. Next five sets of these blends were prepared on an internal mixer. The mixing conditions in internal mixer (Tab. 3) had been chosen experimentally. The higher temperature or higher speed couldn’t...
be used because of rubber degradation. Torque and temperature were measured during mixing. First, NR was masticated alone in the case of NR/BR blends. BR was added after 1 minute.

**Testing**

In these blends the influence of mixing conditions on Mooney viscosity, morphology and glass transition temperature ($T_g$) has been monitored. Morphology micrographs has been obtained by scanning electron microscope Tescan Vega 3 LMU (manufacturer – Tescan a.s.). The secondary electron detector was used. Molded sheets (thickness – 2 mm) were cooled with liquid nitrogen. Then the frozen samples were broken. SEM was performed on the fracture surface. Mooney viscosity ML (1+4) 100 °C of blends was measured on the variable Mooney viscosimeter V-MV 3000 (manufacturer – Montech Werkstoffprüfmaschinen GmbH). For determination $T_g$ Differential scanning calorimeter DSC 2920 modulated DSC (manufacturer – TA instruments) was used. Parameters of DSC analysis: sample weight ≈ 5 mg, temperature range - 150 °C - 20 °C, temperature rate 10 K min⁻¹.

**Results and discussion**

**Influence of mixing conditions on Mooney viscosity**

NR/BR blends with high content of NR prepared on two roll mill has significantly lower Mooney viscosity than blends of the same composition prepared on internal mixer. Figure 2 shows the dependence of Mooney viscosity on the formulation of NR/BR blends prepared on the two roll mill. The higher is NR content in a blend the lower is the Mooney viscosity. This fact can be explained by favorable conditions for NR mastication during mixing.

Mooney viscosity of NR (blend N100B0) decreased from a value of 110 ML (1+4) 100 °C to value 22 ML (1+4) 100 °C.

**Glass transition temperatures**

<table>
<thead>
<tr>
<th>Blend</th>
<th>Mixing conditions</th>
<th>$T_g$ [°C] ML 100 °C</th>
<th>$T_g$ [°C] ML 100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>N60B40</td>
<td>two roll mill, 5 min</td>
<td>-104</td>
<td>-61</td>
</tr>
<tr>
<td>N60B40</td>
<td>internal mixer, 20 min, 20 min</td>
<td>-103</td>
<td>-61</td>
</tr>
<tr>
<td>N60B40</td>
<td>internal mixer, 30 min, 20 min</td>
<td>-104</td>
<td>-62</td>
</tr>
<tr>
<td>N60B40</td>
<td>internal mixer, 40 min, 20 min</td>
<td>-104</td>
<td>-61</td>
</tr>
<tr>
<td>N90B10</td>
<td>internal mixer, 30 min, 20 min</td>
<td>-107</td>
<td>-62</td>
</tr>
<tr>
<td>N10B90</td>
<td>internal mixer, 30 min, 20 min</td>
<td>-104</td>
<td>-62</td>
</tr>
<tr>
<td>S50B50</td>
<td>two roll mill, 5 min</td>
<td>-107</td>
<td>-53</td>
</tr>
<tr>
<td>S50B50</td>
<td>internal mixer, 30 min, 20 min</td>
<td>-106</td>
<td>-52</td>
</tr>
</tbody>
</table>

**Fig. 1:** The dependence of temperature on mixing time NR/BR blends at rotors speed of internal Brabender mixer 30 min⁻¹.

**Fig. 2:** Comparison Mooney viscosities of NR/BR blends prepared on a laboratory two roll mill, mixing time 5 min.

**Fig. 3:** Comparison Mooney viscosities of NR/BR blends after 20 min mixing on an internal Brabender mixer at rotors speeds 20, 30 a 40 min⁻¹.

**Fig. 4:** Comparison Mooney viscosities SBR/BR blends prepared on laboratory two roll mill, mixing time 5 min.
Mooney viscosity of the NR/BR blends prepared on internal mixer has slightly descending trend (Fig. 3). The mastication of NR is inhibited by an oxygen lack and absence of plasticizers. The mixing temperature was ranged between 90 and 100 °C during mixing (Fig. 1). Mastication is not effective at these temperatures. SBR and BR are produced in processable state. Decrease of their Mooney viscosity is not so significant. Mooney viscosity of SBR/BR blends prepared on the two roll mill increases with decreasing content of SBR (Fig. 4). Mooney viscosity of blends containing from 0 to 60 % SBR is essentially independent on mixing conditions (Fig. 5).

Influence of mixing conditions on blends morphology
The secondary electron detector was used for acquirement of micrographs showing blends morphology. Already during NR/BR blends mixing, it was evident that the resulting material will be heterogeneous. Rubbers tried to separate when they get in touch with each other. SEM micrographs confirmed heterogeneity. It is impossible to say, which phase is NR and which is BR. Blends with higher content of NR seem to be more heterogeneous (Fig. 6). Micrographs of blends mixed under various conditions exhibit no noticeable differences (Fig. 7, 8). It follows that adjustment of conditions failed to achieve greater homogeneity.

The behavior of SBR/BR blends was totally different. Rubbers were readily mixed. From micrographs, it seems that these blends are homogenous (Fig. 9–11). But it is more likely, that SBR/BR blends are heterogeneous with very small domains. SEM is not able to distinguish them.

Influence of mixing conditions on glass transition temperature
For each blend were gained two values of $T_g$ (Tab. 3) corresponding with values of $T_g$ themselves rubbers ($T_g^{NR} = -61 °C$, $T_g^{BR} = -104 °C$ and $T_g^{SBR} = -52 °C$). Only the size of the peaks of the derivative curve was changed depending on the contents of rubbers in blends. It follows that neither of SBR and BR were mixed on molecular
level. DSC analysis proved, that NR/BR and SBR/BR blends are immiscible.

Conclusion
The results from DSC and SEM show that NR, BR and SBR are immiscible. $T_g$ values are independent on the mixing method as well as the composition of blends. It was found that SEM is not too suitable for studying morphology of these blends. The SBR/BR blends seem to be homogeneous, but DSC proves that it is not true. Only Mooney viscosity measurements proved their dependence on the method of mixtures preparing. The question remains whether the increased homogeneity could be achieved through vulcanization.

References