ELASTOMERS BASED ON NR/BR/SBR TERNARY RUBBER BLEND: MORPHOLOGICAL, MECHANICAL AND THERMAL PROPERTIES

Article Highlights
• The influence of amount SBR rubber in NR/BR/SBR rubber blends was investigated
• The amount of the CB in NR/BR/SBR rubber blend is 60 phr
• The NR/BR mass ratio in ternary nano-blends is 1:1
• The optimum content of SBR rubber in NR/BR/SBR rubber blend is 40 phr

Abstract
The elastomeric materials based on NR/BR/SBR ternary rubber blend were investigated. The polyisoprene (NR), butadiene (BR) and styrene butadiene (SBR) rubbers were used as network precursors and carbon black (CB) as an active filler (60 phr) for elastomeric materials preparation. For sample preparation, the mass ratio of NR to BR was constant, 1:1, but the SBR content was varied from 0 to 80 phr. The morphological, mechanical and thermal properties of prepared elastomeric materials were determined using scanning electron microscopy (SEM), mechanical tensile measurements and thermogravimetric analysis (TGA). Mechanical properties were assessed before and after thermo-oxidative aging during 168 h at 100 °C. The values of tensile strength, elongation at break, and hardness decrease up to 40 phr of SBR content and after that are increasing, but abrasion resistance of ternary rubber blends increases. The thermal decomposition temperature obviously shifted to a higher temperature for the sample with 40 phr of SBR.

Keywords: carbon black, mechanical properties, ternary rubber blends, thermo-oxidative aging, thermal properties.

One of the most effective methods for developing new polymer materials is polymer blending. This way of creating new materials has been used for over two decades and has been of great importance for science and industry [1]. From the industrial point of view, mixtures of elastomers have multiple applications, reducing the cost of making products improve the flow [2]. The most commonly used tire rubbers are natural rubber (NR), styrene-butadiene rubber (SBR) and polybutadiene rubber (BR). Great use of natural rubber (cis-1,4-polyisoprene) in the elastomeric materials for tires is due to its effect on dynamic properties as a result of high stereoregular microstructure and the free rotations around the methylene C-C bond [3]. An important factor in the rubber blending is the solubility parameter. A big difference in the solubility parameters gives an inhomogeneous blend. NR and SBR have similar solubility parameters (both close to 10.0). According to [4], fatigue and cracking of elastomeric materials based on NR rubber can be improved by adding small amounts of SBR rubber. Many studies showed that the mechanical properties of such a blend can be significantly enhanced by adding an appropriate compatibilizer [5]. Mixing of SBR with NR may improve the tensile strength [6]. Mohan et al. studied the influence of nano-clay on the tensile strength, hardness, tear and heat stability of NR/SBR blends [7]. Making the interior of wetting the
filler, and its dispersion in the polymer matrix, as well as filler-polymer interaction, increases the mechanical and electrical properties of the CB polymer composites [8]. Carbon black (CB) with unique nanoscale structure combined with the high strength of the carbon-carbon bondings and a large aspect ratio opens up a wide range of new applications. However, the physical properties of the CB-polymer composites are often below expectations, because a sufficiently efficient force transfer between the polymer matrix and CB has not yet been reached. To take advantage of excellent mechanical and electrical properties of CB in polymer composites, internal wetting and dispersion of the filler in the polymer matrix must improve [8]. It is known that the smaller the contact angle between the polymer and filler, the better the wetting of fillers and stronger polymer-filler interaction can be obtained. Although the contact may be calculated from the surface tension of the individual components of the mixture, is not sufficient for description of the complex filler polymer wetting process [9]. Analysis of rubber-filler gel after extraction experiments (bound rubber measurement) by means of nuclear magnetic resonance (NMR), pyrolysis gas chromatography (PGC) and Fourier-transform infrared spectroscopy (FTIR), as well as thermogravimetric analysis (TGA), was carried out for qualitative and quantitative characterization of the physical background of the filler-polymer interaction in carbon black or silica-filled rubber compounds [10]. If the rubber blend consists two or more rubbers, the bonding filler aggregate with rubber is different because of their affinities [11].

The goal of this applicative work was to prepare carbon black reinforced elastomers based on three network precursors: polyisoprene (NR), polybutadiene (BR) and styrene butadiene (SBR). The effect of SBR rubber content on its mechanical properties and thermal stability was also determined.

EXPERIMENTAL

Materials

Materials used in this manuscript are the same as the ones used in manuscript [12]. For sample preparation, the NR to BR rubber mass ratio was constant, 1:1, while the SBR rubber content was varied from 0 to 80 phr. Six samples of NR/BR/SBR ternary rubber blends (50/50/0; 40/40/20; 30/30/40; 25/25/50; 20/20/60 and 10/10/80 mass ratio) reinforced with 60 phr of CB were prepared. The curing system contained: CBS (1.4 phr); diphenylguanidine, DPG (1 phr); N-(cyclohexylthio)phthalimide, CTP 100 (0.2 phr) and sulfur (2 phr). The content of zinc oxide was 3 phr. The content of stearic acid was 2 phr. The content of the naphthenic oil was 10 phr. Formulations of rubber compounds are shown in Table 1.

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<tr>
<th>Composite NR/BR/SBR/CB (phr)</th>
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Sample preparation

The samples have been prepared as described elsewhere [13]. In all rubber blend compounds, the NR/BR rubber mass ratio was 1:1, but SBR rubber content was variable 0-80 mass%.

Curing characteristics determination

The cure rate index (CRI) is determined according to the equation presented elsewhere [13]. The rheological properties were determined according to literature [12].

The cross-linking was carried out in an electrically heated hydraulic press (E-604 Metrohm Herisau) under a pressure of 20 MPa and temperature of 160 °C, during optimum cure time, t90.

Characterization of obtained materials

Tensile testing machine (Instron 4301) was used to determine tensile strength and elongation at break percentage according to ASTM D412 method [14]. The failures of materials were calculated using the equations presented in [15]. The hardness of rubber blends was determined according to ASTM D2240 method [16]. Abrasion test was conducted using the ASTM D5963 test method [17] and represents the corresponding loss of volume of rubber in mm³. The thermo-oxidative characteristics (tensile strength, elongation at break and hardness) of the vulcanized rubber blends were studied after aging of 168 h at 100 °C according to ASTM D573 [18]. The thermal stability of NR/BR/SBR rubber blends composites were determined according to [12]. The morphological characteristics of the blend were observed by scanning electron microscopy (JEOL JSM 5300) and samples were prepared according to the publication [12], with magnification of 500x.

* Mass part per hundred mass parts of rubber.
RESULTS AND DISCUSSION

Curing characteristics

The curing characteristics for NR/BR/SBR ternary rubber blends were determined at 160 °C and optimum cure time, $t_{90}$. The mechanical properties are also responsible for the quality of rubber products for any use [12]. When the content of SBR rubber in NR/BR/SBR rubber blends is increasing, the values of $M_l$ and $M_h$ are decreasing up to 40 phr, after that, the slight increase of their values was observed. $M_h$ values indicate the presence of the crosslinking process in rubber compounds. Also, the values of $t_{90}$ and $t_s$ decrease down to 40 phr of SBR rubber content.

The effect of SBR rubber content on scorch time $t_s$ and cure time, $t_{90}$, for NR/BR/SBR ternary rubber blends composites are shown in Figure 1.

Figure 1c shows the influence of SBR rubber content on CRI values of NR/BR/SBR ternary rubber blend composites. CRI values increase with the SBR rubber content increased up to 20 phr and after that decrease. SBR rubber was originally developed as an elastomer of general purpose and is the most commonly used elastomer in the world. Its largest application is in the manufacture of a treadmill of passenger tires, in the footwear industry, cable industry, hose making, etc. SBR in comparison with natural rubber has better heat and abrasion resistance. During the extrusion process, the SBR extrusion is smooth and its shape remains unchanged for a long time [19].

Morphology of prepared materials

The fractured surface of composites based on NR/BR/SBR/CB (40/40/20/60) ternary rubber blend is displayed in Figure 2. SEM micrograph shows the presence of a hole as a result of poor transmission of the stress between the rubber chains and CB filler. The low polarity of the rubber matrix and the high energy surface of CB result in poor compatibility and contact between the matrix and the filler [21].

Mechanical properties

The effect of SBR rubber content on mechanical properties (tensile strength, elongation at break, hard-
Figure 2. SEM micrograph of elastomeric materials based on NR/BR/SBR/CB (40/40/20/60) ternary rubber blend at 500× magnification.

Figure 3. Mechanical properties of elastomeric materials based on ternary NR/BR/SBR/CB rubber blend before and after aging (100 °C for 72 h and 168 h): tensile strength (a), elongation at break (b), hardness (c) and abrasion (d).

Tensile strength and elongation at break. However, an improvement in elongation at break is found when the three rubbers were used together [22]. The tensile strength decreases gradually with SBR rubber content increasing in rubber blends up to 40 phr, and then increases (Figure 3a). The NR/BR/SBR (10/10/80) rubber blend has the lowest values for tensile strength. NR is a kind of polymer that includes cis-1,4-polyisoprene and trans-1,4-polyisoprene, and the trans type has lower strength than the cis type, so it reduces tensile property when NR is replaced with SBR in ternary blends [23]. The hardness values (Figure 3b) have similar behavior as tensile strength for NR/BR/SBR ternary rubber blend.

The elongation at break shows the opposite trend to tensile strength. The values of elongation at break for NR/BR/SBR ternary rubber blend reduced up to 20 phr of SBR rubber content. The NR/BR/SBR rubber blend as a system might have a porous structure, according to that the elongation at break of composites without SBR is higher than with SBR (Figure 3c). Figure 3d shows the effect of SBR rubber content.
on abrasion loss of NR/BR/SBR rubber blend composites. It can be seen that abrasion loss increases with SBR rubber content increase in NR/BR/SBR rubber blends. SBR is the copolymer of butadiene and styrene, and their group acts as a harder block to increase the degree of abrasion loss of blends. Gradually, a poor abrasion resistance of rubber blends can be observed (Figure 3d).

By the addition of a small amount of SBR rubber, the disturbance of the NR/BR rubber blend homogeneity [24] can happen and mechanical properties values are reduced. The sample with a greater content of SBR has lower values for tensile properties.

Thermo-oxidative aging

The aging process is defined by a set of irreversible physical and chemical changes in the observed material. During the aging process the rubber’s mechanical properties become worse, due to variations in the primary structure of the polymer. The final properties of crosslinked materials strongly depend on the structure of cross-connections [12,25]. Figure 3a–c show the effect of SBR rubber content on the mechanical properties of thermo-oxidative aging. After aging (at 100 °C during 168 h) the tensile strength values of the NR/BR/SBR ternary rubber blend composition decrease to 30/30/40 composition and then increase with SBR rubber content increase. The elongation at break, hardness and abrasion loss of carbon black filled NR/BR/SBR rubber blend tend to decrease with SBR content increase, due to the post-curing effect. During the thermo-oxidative degradation, loss reactivity and SBR dilution in NR/BR can be observed [3]. Disturbance of the elasticity of the rubber chain after aging enlarged the material stiffness.

Thermal stability of prepared materials

Thermal degradation of rubbers is molecular deterioration as a result of overheating. Thermal stability is one of the most important characteristics for a broad range of elastomer applications [11]. At high temperatures, the components of the polymer network chains can be broken (chain scission) and react with one another to change the properties of the material. Thermal stability can be defined as an upper limit to the service temperature, as much as the possibility of mechanical property loss. Indeed, without additives, significant deterioration can occur at temperatures much lower than those at which mechanical failure occurs. The reactions involved in degradation lead to optical and physical property changes relative to the initial properties. Lee et al. [26] investigated the thermal stability of elastomers based on NR, SBR and BR rubbers.

Figures 4a and b show the thermal degradation of CB filled ternary rubber blend composites. DTG data of peak values and mass loss at different temperatures are summarized in Table 2.

Thermal degradation of NR/BR/SBR ternary rubber blends with 60 phr of CB (Figure 4a and Table 2) goes on in two steps: the first decomposition step is the volatilization of processing oil or any other low-boiling-point components (200–400 °C) with mass loss of 14.3-11.7 wt.%. The second decomposition stage occurs at temperature region from 400 to 500 °C. However, in Figure 4b, for all samples, we can see that there is an overlap of the peaks. This is influenced by the co-vulcanization process [27]. On the DTG thermograms for all samples (Figure 4b) the two DTG peaks appear smaller from 373.6 to 387.9 °C and from 433.8 to 446.4 °C, respectively. The second peak originated from the degradation process of...
the NR rubber, and mass loss of 53.2-44.4 wt.% can be noticed. For composites with SBR rubber, well-defined peaks are increasingly fusing in the other larger peak (Figure 4b). When the amount of the SBR rubber increases in prepared composites, the thermal decomposition temperature shifts to a higher temperature (Figure 4b and Table 2).

Degradation of NR led to isoprene and dipentene, and that of SBR led to a large number of products, like 4-vinyl cyclohexene, styrene and methylbenzene [28].

CONCLUSION

In this applicative work, six types of carbon black reinforced ternary rubber blend NR/BR/SBR were prepared. This type of elastomeric material based on three network precursors is used for tire carcasses. The mass share of NR and BR in obtained materials was constant 1:1 and the SBR content was varied from 0 to 80 phr. It was estimated that the cure characteristics (M₁ and M₉, and t₉₂ and t₉₀), assessed CRI values and mechanical properties of obtained samples mainly depend on the amount of SBR rubber in the composite materials. Maximum values of M₁ and M₉ have NR/BR/SBR/CB (50/50/0/60), and they are 7.2 and 2.1 dNm. For t₉₂ and t₉₀ maximum values have NR/BR/SBR/CB (50/50/0/60) also, and they are 0.31 and 0.61 min. When SBR rubber content increases the values of M₁ and M₉, t₉₂ and t₉₀ decrease to NR/BR/SBR/CB (30/30/40/60) rubber blend composites.

Tensile strength and hardness decreased gradually with SBR rubber content increase. Maximum values are obtained at NR/BR/SBR/CB (50/50/0/60) rubber blend composites (19 MPa before and 7 MPa after aging; 36 Sh-A before and 45 Sh-A after aging). The values of elongation at break decrease with SBR rubber content increase. Minimum values have NR/BR/SBR/CB (40/40/20/60) rubber blend composite (350% before and 150% after aging). The abrasion resistance increases with SBR rubber increase. The minimum values have NR/BR/SBR/CB (40/40/20/60) rubber blend composites (210 mm³ before aging) and NR/BR/SBR/CB (20/20/60/60) rubber blend composites (240 cm³ after aging).

The SEM micrograph of NR/BR/SBR/CB (40/40/20/60) samples shows a rough surface with many tear lines, and branching indicates higher tensile strength. The thermal degradation temperature shifts to a higher temperature up to 40 phr of SBR rubber content (NR/BR/SBR/CB 30/30/40/60). The properties of a vulcanized rubber can be significantly influenced by details of the compounding. Rubber ingredients can have an influence on the physical and chemical stability of the finished material.

Acknowledgment

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REFERENCES

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ELASTOMERI NA BAZI NR/BR/SBR TRIBLENDE: MORFOLOŠKA, MEHANIČKA I TERNIČKA SVOJSTVA

Ispitivani su elastomerni materijali na bazi NR/BR/SBR triblende. Kao prekursori mreža, za pripremu elastomernih materijala, korišćeni su poliizoprenski (NR), polibutadienski (BR) i polistiren-butadienski (SBR) kaučuki ojačani čađom (CB) kao aktivnim punilom (60 phr). Maseni odnos sadržaja NR i BR kaučuka je bio konstantan 1:1, dok je sadržaj SBR kaučuka menjan od 0 do 80 phr. Morfološka, mehanička i termička svojstva pri-premljenih elastomernih materijala određivana su korišćenjem skenirajuće elektronske mikroskopije (SEM), termogravimetrijske analize (TGA) i merenje mehaničkih svojstava. Mehanička svojstva su ispitivana pre i posle termo-oksidacionog starenja u toku 168 h na 100 °C. Vrednosti prekidne čvrstoće, prekidnog izduženja i tvrdoće za NR/BR/SBR triblende opadaju do sadržaja SBR kaučuka od 40 phr, a nakon toga se povećavaju. Otpornost na abraziju NR/BR/SBR triblenda se povećava sa povećanjem sadržaja SBR kaučuka. Temperatura termičkog razlaganja za NR/BR/SBR triblende se povećava sa povećanjem sadržaja SBR kaučuka i maksimalnu vrednost dostiže kod NR/BR/SBR triblende sa sadržajem SBR kaučuka od 40 phr.

Ključne reči: čađ, mehanička svojstva, triblende, termo-oksidaciono starenje, termička svojstva.