Effect of ethanol-assisted mixing on the selected properties and homogeneity of NR/BR blends

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DOI: https://doi.org/10.14314/polimery.2023.3.2

Abstract: The effect of the mixing method (normal and ethanol-assisted) on selected properties of natural rubber with butadiene rubber blends (NR/BR 80/20) was investigated. Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) were used to evaluate the properties. In addition, the mechanical tensile properties, tear resistance and thermal aging, as well as vulcanization characteristic were determined. It was found that ethanol-assisted mixing can significantly improve the mechanical properties and thermal stability of the blends as a result of better dispersion of additives in the rubber matrix.

Keywords: natural rubber, butadiene rubber, blends, dispersion.

Wpływ mieszania wspomaganego etanolem na wybrane właściwości i jednorodność mieszanek NR/BR

Streszczenie: Zbadano wpływ metody mieszania (tradycyjna i wspomagana etanolem) na wybrane właściwości mieszanin kauczuku naturalnego z kauczukiem butadienowym (NR/BR 80/20). Do oceny właściwości zastosowano skaningową mikroskopię elektronową (SEM), spektroskopię w podczerwieni z transformacją Fouriera (FTIR) oraz analizę termograwimetryczną (TGA). Ponadto oznaczono właściwości mechaniczne przy rozciąganiu, odporność na rozdzieranie i starzenie termiczne, a także właściwości wulkanizacyjne. Stwierdzono, że mieszanie wspomagane etanolem może znacząco poprawić właściwości mechaniczne i stabilność termiczną mieszanin NR/BR, jako efekt lepszej dyspersji dodatków w osnowie gumowej.

Słowa kluczowe: kauczuk naturalny, kauczuk butadienowy, mieszaniny, dyspersja.

Natural rubber (NR) is a natural polymer that can be extracted from rubber trees. 91 to 94% of the components are hydrocarbons (namely cis-1,4-polyisoprene) while the rest mainly consists of non-protein, fatty acid, ash, sugar, and other non-rubber substances. NR has excellent characteristics, which include low hysteresis, high insulation, and high durability. Therefore, it is widely used in daily life, medical care, transportation, agriculture, meteorological measurement, and other fields [1–3]. It is precisely due to the natural properties of rubber that it is widely used in various fields [4–7].

Cis-polybutadiene rubber (BR) is the second most used rubber in the world [8–12]. Its properties can be modified by improving the synthesis procedure as well as adjusting the catalyst amount used to form better wear resistance. Currently, the demand for high quality cis-polybutadiene rubber is increasing significantly, so a constant improvement in synthesis process and catalyst types is necessary. BR is characterized with relatively low tensile and compressive strength, poor dimensional stability as well as high industrial production costs. The stress induced crystallization of cis-polybutadiene rubber is also lower than that of natural rubber [13].

With increase of demand, the performance requirements for rubber products are constantly increasing. The excellent efficacy of a single rubber product is not enough

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to meet the industry's needs. Therefore, blends of two or more types of rubbers have been developed.

To combine excellent properties and compensate rubbers disadvantages, more and more researchers are focusing on rubber blends.

Rubber products are widely used in various areas of life. Rubber formulations are varied and contain different additives with adjustable properties as well as different physical and chemical properties. Therefore, it is a big challenge to ensure a homogeneous dispersion of additives in the rubber matrix [14, 15].

In this study, we have investigated the influence of ethanol-assisted mixing on the homogeneity and physical properties of natural rubber and cis-polybutadiene rubber (NR/BR 80/20) blends. Three formulas were selected to prepare NR/BR blends: i) conventional, ii) high sulfur low accelerator, and iii) low sulfur high accelerator. The additives, after being mixed with anhydrous ethanol, were air-dried, and then ground into a homogeneous powder. It was assumed that this would increase their miscibility with the rubber matrix, improving interactions at the interface. The structure, thermal and mechanical properties of the obtained NR/BR blends were evaluated by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, and thermogravimetric analysis (TGA).

EXPERIMENTAL PART

Materials

A commercial natural rubber (NR, SCR5), and cis-polybutadiene rubber (BR, GB 8659-1988) were purchased from Qingdao Xiangtaixing Rubber Co., Ltd. (China). Zinc oxide (ZnO), stearic acid (SA), n-isopropyl-n'-phenyl-p-phenylenediamine (4010NA), n-cyclohexyl-2-benzothiazole sulfonamide (CZ) and sublimation sulfur (S) were provided by Shandong Baiqian Chemical Co., Ltd. (China).

Methods

Vulcanization characteristics was determined according to GB/T16584 standard using flat vulcanizer (25 tons QLB 350×350×2, Shanghai Rubber Machinery Factory, China). The chemical structure was analyzed by Fourier transform infrared (FTIR) spectroscopy (FTIR-1500, Zhongshi Walker Technology Development Co., Ltd, China) using the KBr pellet method. The spectra were recorded using at least 64 scans with 4 cm^{-1} resolution, in the spectral range

The fracture surfaces of NR/BR blends were observed by scanning electron microscopy (SEM) under high vacuum with a scanning electron microscope (JSM-2000EX, Joel, Japan) operating at 15 kV. The samples were prepared by brittle fracturing under liquid nitrogen. The tensile properties and tear strength were tested using electronic tensile machine (DXLL-50000, Shanghai Dejie Instrument Equipment Co., Ltd, China) according to GB/T528 and GB/T529 standards, respectively. Aging tests were performed at 60°C for 120 h using a jet dryer (type 101-3A, Tianjin Taist Instrument Co., Ltd, China).The thermal stability was determined with a thermogravimetric analyzer (TG 209F3, Shanghai Instrument Technology Co., Ltd, China). The samples were heated from 25°C to 800°C at a rate of 5°C/min in a nitrogen atmosphere.

Preparation of NR/BR blends by standard method

First, NR and BR (80/20) were mixed in two-roll mill (type XK-160B, Shanghai Light Industry Machinery Co., Ltd., China). Then the mixture was plasticized with the addition of activators (SA, ZnO), antioxidant (*N*-isopropyl-*N*'-phenyl-p-phenylenediamine) and accelerator (*N*-cyclohexyl-2-benzothiazolesulfonamide). After the additives were dispersed, further mixing was continued with the vulcanizing agent (sublimation sulfur). The roll pitch was set to 0.5 to 1 mm and the thin-walled sheet was passed six times, then the adjustment was changed to 1 to 2 mm with a triangular wrapper installed and passed 4 times. The vulcanizate formulas are shown in Table 1.

Preparation of NR/BR blends by ethanol-assisted mixing

Additives were weighed into the beaker and then absolute ethanol was added and stirred for 10 min using a cantilever electric stirrer. The contents were allowed to stand and dry, then ground in a mill. In the next stage, the mixture of NR and BR was plasticized with the addition of powdered additives in a two-roll mill. The process was continued as in the standard method.

T a b l e 1. Vulcanizate formulas

Formula	NR, wt%	BR, wt%	ZnO, wt%	SA, wt%	4010NA, wt%	CZ, wt%	S, wt%
Conventional (formula 1)	80	20	5	2	1	1.5	2
High sulfur/ low accelerator (formula 2)	80	20	5	2	1	0.6	3
Low sulfur/ high accelerator (formula 3)	80	20	5	2	1	3	0.5

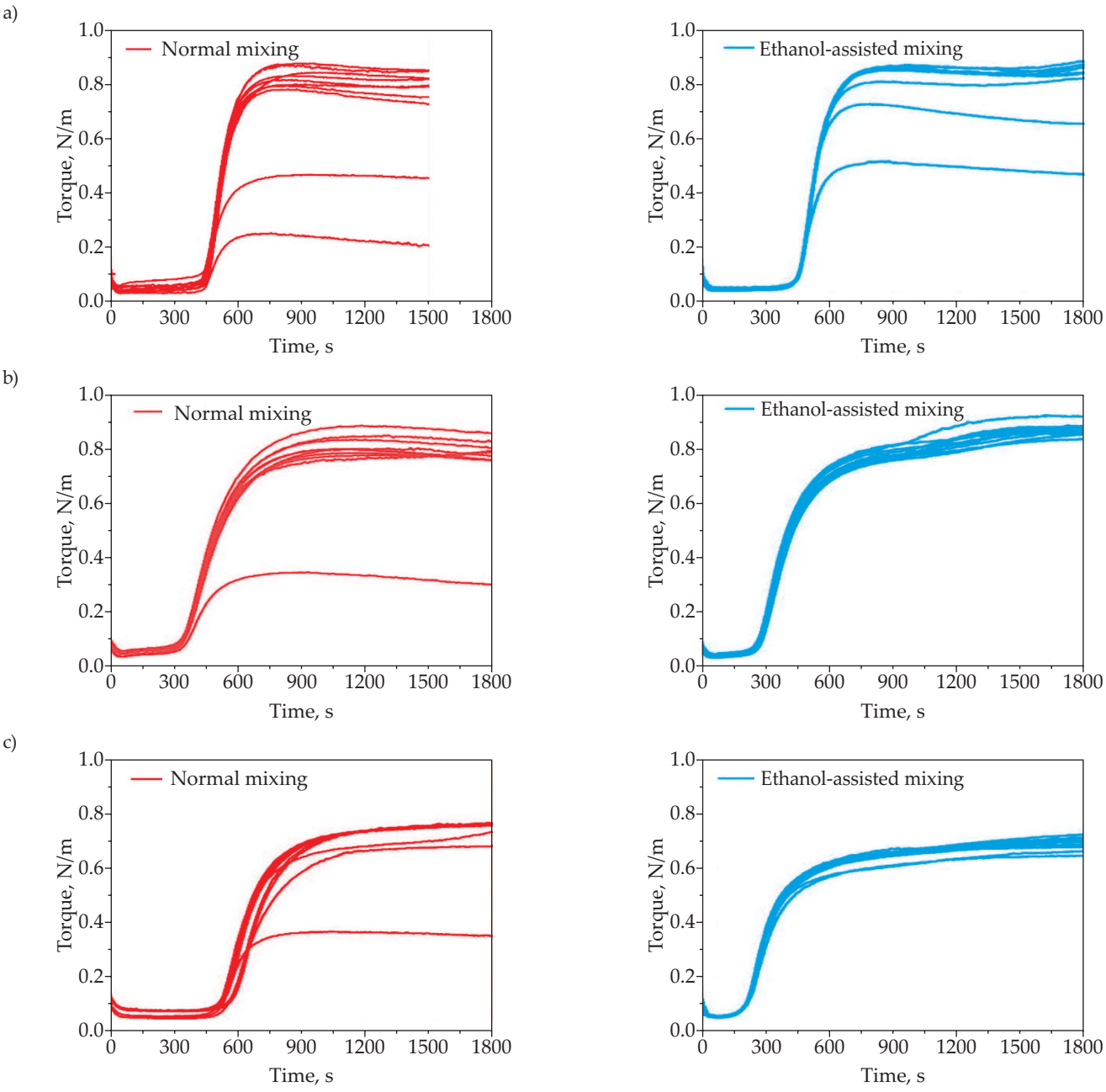

Fig. 1. Vulcanization curves of NR/BR blends: a) formula 1, b) formula 2, c) formula 3

RESULTS AND DISCUSSION

Vulcanization characteristics of NR/BR blends

Figure 1 presents the vulcanization curves of NR/BR blends obtained by normal mixing and ethanol-assisted mixing according to the conventional, high sulfur low accelerator and low sulfur high accelerator formulas. Each graph is superimposed and mentions data obtained from ten samples. The overlapping degree of vulcanization curve after ethanol-assisted mixing is significantly higher than that of normal mixing, which indicates that ethanol-assisted mixing makes additives uniformly dispersed in the rubber matrix. The uniform mixing of additives and rubber matrix increased the crosslinking density of NR/BR blends, while the ethanol-assisted mixing method improved the homogeneity of the colloids.

It is clear from Fig. 1 that the scorch time (T_{10}) of the ethanol-assisted mixing was shorter than that of the normal mixing, indicating that reducing the positive vulcanization time (T_{90}) accelerated the vulcanization rate and improved colloid strength. At the same time, the curing speed (V_C) of the vulcanizate prepared by mixing with ethanol significantly increased, as did the average value of the maximum torque (F_{Max}), while the minimum torque (F_L) decreased, and the rubber fluidity improved [16–19]. Therefore, after ethanol-assisted mixing, the compatibility of the additives with the rubber matrix and the cross-linking density were enhanced. Ethanol-assisted mixing made the sulfur dispersion more homogeneous, and the vulcanization activity was

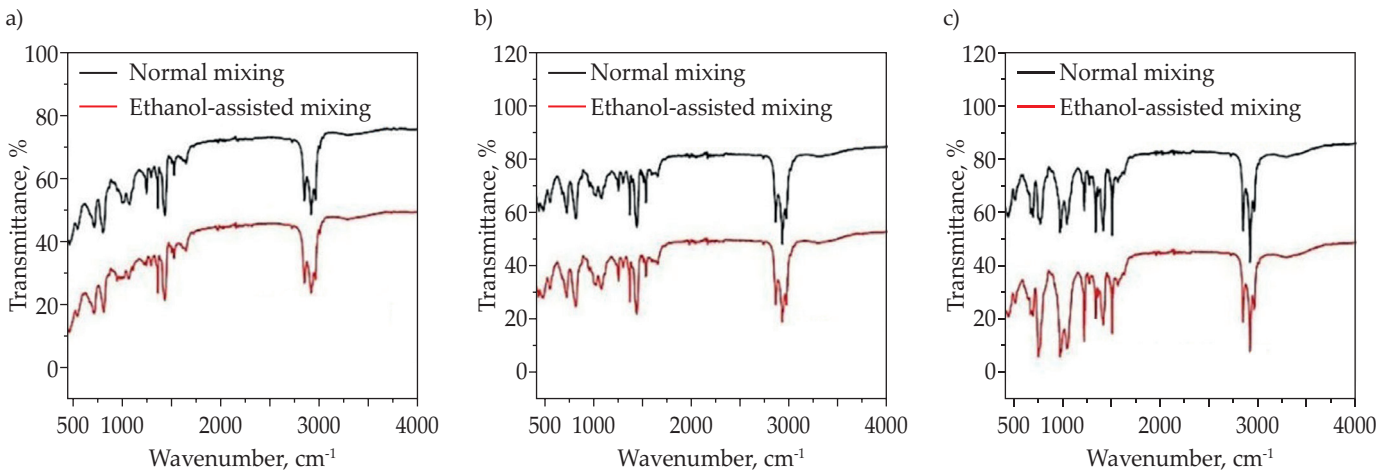

Fig. 2. IR spectra of NR/BR blends: a) formula 1, b) formula 2, c) formula 3

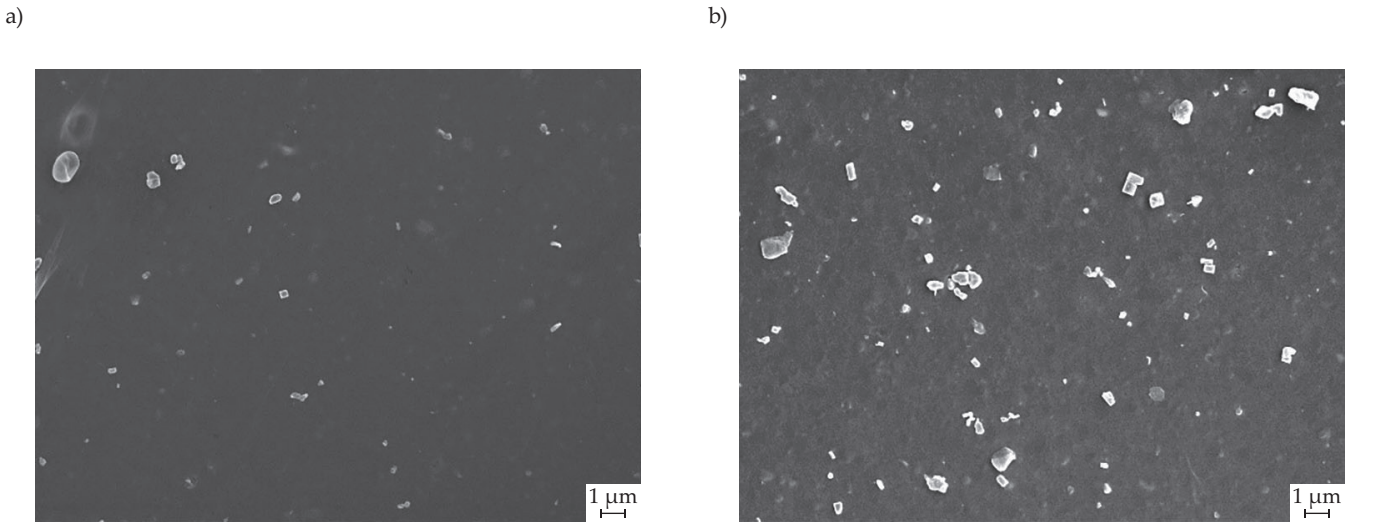

Fig. 3. SEM images of NR/BR blend obtained according to the conventional formula: a) normal mixing, b) ethanol-assisted mixing

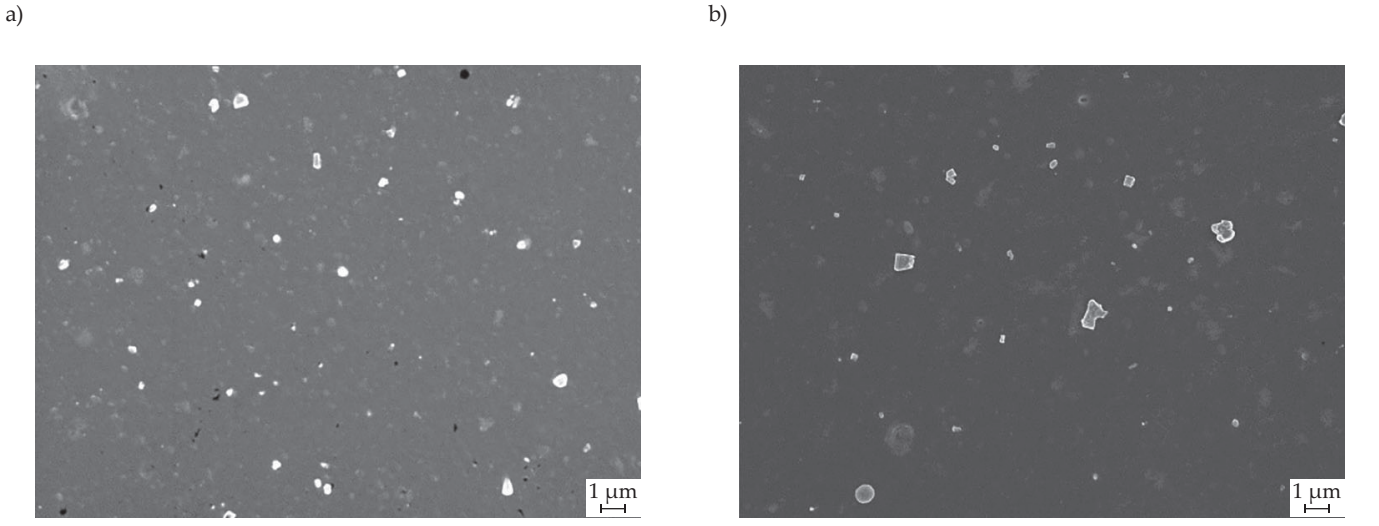

Fig. 4. SEM images of NR/BR blend obtained according to the high sulfur formula: a) normal mixing, b) ethanol-assisted mixing

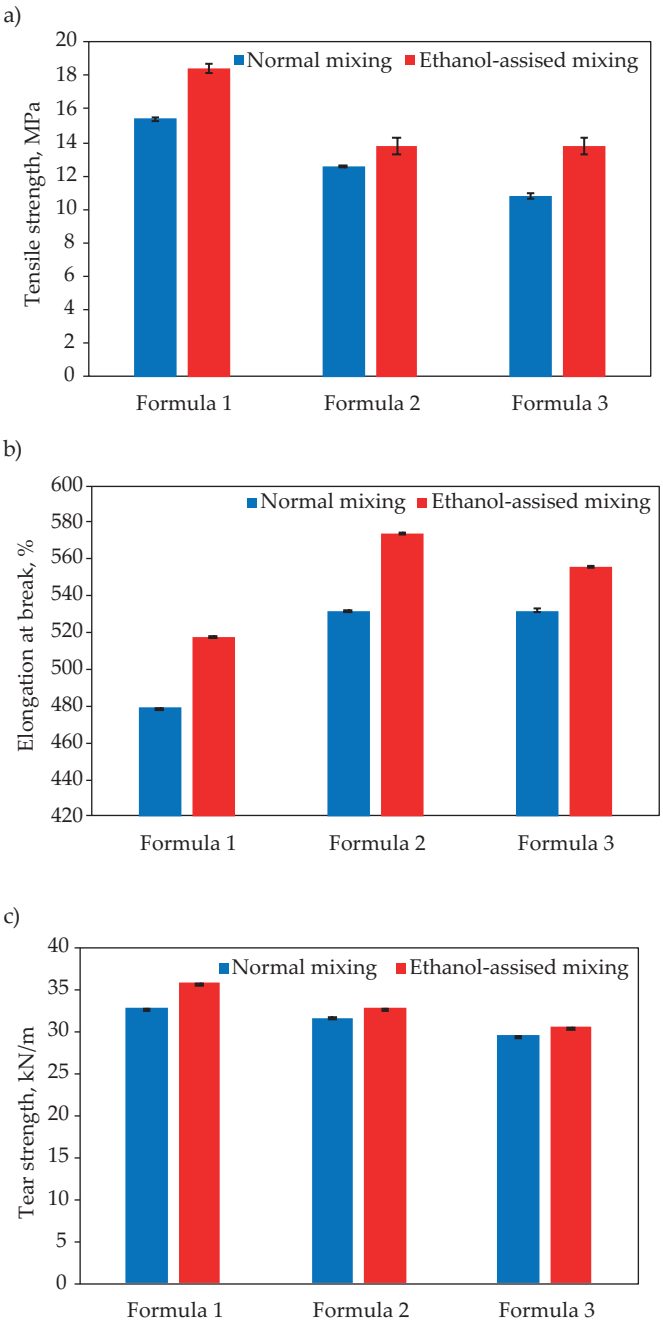

Fig. 5. Mechanical properties of NR/BR blends: a) tensile strength, b) elongation at break, c) tear strength

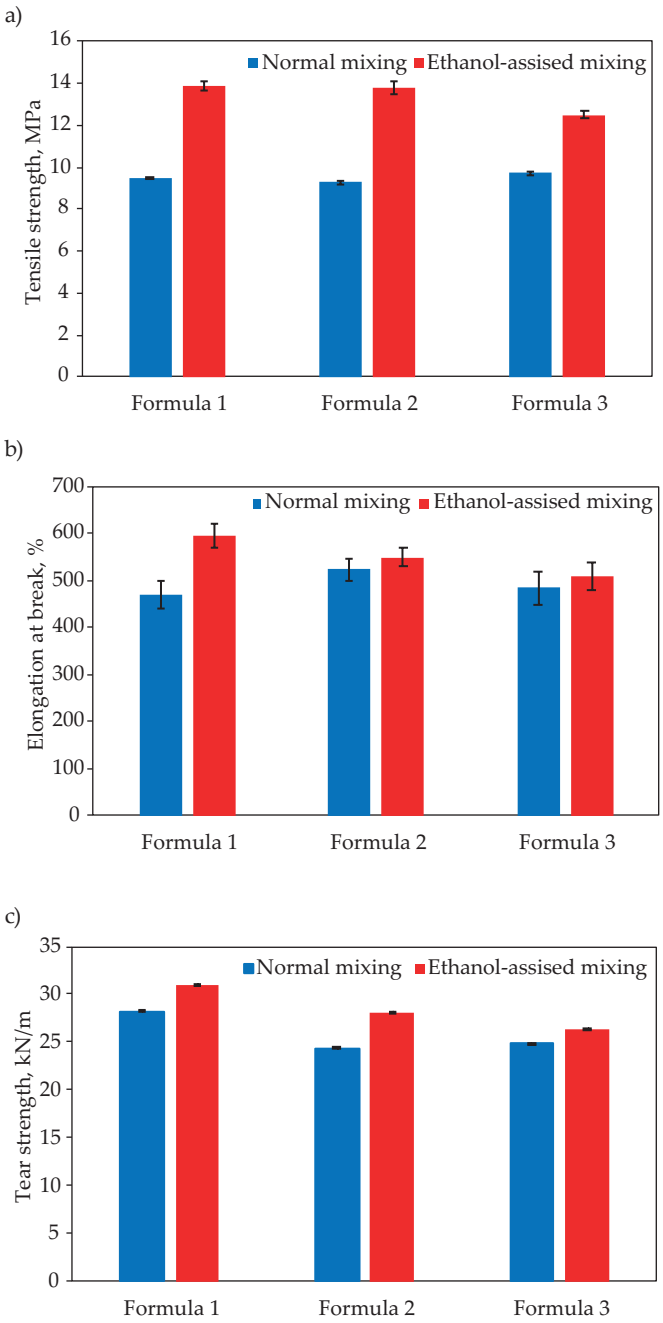

Fig. 6. The effect of thermal aging on the mechanical properties of NR/BR obtained by normal and ethanol-assisted mixing according to three formulas

improved during the process. The improved characteristics therefore included the performance properties of vulcanizates prepared by mixing with ethanol, vulcanization parameters and the compatibility of additives with rubber.

Infrared analysis of NR/BR blends

Figure 2 presents the FTIR spectra of NR/BR blends. In the case of blends obtained according to formula 1 and 2, no significant differences in the IR spectra were found, regardless of the mixing method. On the other hand, much bigger differences in the intensity of the peaks at the wavenumber 800 cm^{-1} and 1260 cm^{-1} were observed for the blend obtained by ethanol-assisted mixing according to formula 3. The peak at 800 cm^{-1} is attributed to the stretching vibrations of C-S bond, while 1260 cm^{-1} to the stretching vibrations of tertiary amine C-N bond [20, 21]. The higher intensity of these peaks for the blend obtained by ethanol-assisted mixing suggests stronger interactions between the rubber matrix and the additives, resulting in better homogeneity.

SEM analysis

Figures 3 and 4 show SEM images of NR/BR blends obtained according to conventional and high sulfur for-

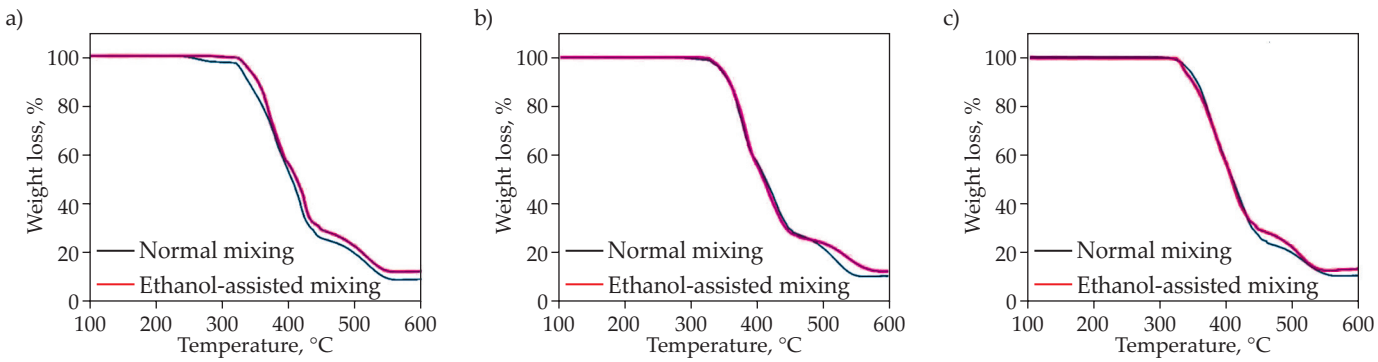

Fig. 7. TGA thermograms of NR/BR blends obtained by normal and ethanol-assisted mixing: a) formula 1, b) formula 2, c) formula 3

mulas, respectively. Darker backgrounds indicate the rubber matrix of NR/BR (80/20) blend, while the white parts represent the additives. In the case of ethanol-assisted mixing SEM micrographs confirm stronger interactions between the rubber matrix and the additives, resulting in better homogeneity (Figs. 3, 4).

Mechanical properties of NR/BR blends

Figure 5 shows the tensile properties and tear strength of the NR/BR blends prepared by normal mixing and ethanol-assisted mixing according to three formulas. Ethanol-assisted mixing improved tensile strength, elongation at break, and tear strength depending on the formulation. The biggest influence of the formula and the method of mixing was found in the case of tensile strength. With ethanol-assisted mixing, the improvement in tensile strength was about 40% (formula 1 and 2).

Thermal aging

The effect of thermal aging on tensile properties and tear strength of NR/BR blends obtained by normal and ethanol-assisted mixing according to three formulas is presented in Fig. 6. After a 120-hour thermal aging at 60°C, the tensile properties and tear strength of all tested rubbers decreased in comparison with the non-aged ones. It is worth emphasizing that the blends obtained by ethanol-assisted mixing were characterized by bigger resistance to aging, as evidenced by better mechanical properties. This may be due to better dispersion of additives in the rubber matrix, which was confirmed by SEM studies.

Thermogravimetric analysis

Figure 7 shows the thermogravimetric curves of NR/BR blends obtained by normal and ethanol-assisted mixing according to three formulas. Comparing the mixing methods, the onset degradation temperature of the ethanol-assisted mixing increases slightly, while the rate of thermal degradation decreases. Mass loss up to 300–350°C is associated with the removal of low volatile components. A further increase in temperature (350–550°C) causes the thermal polymer degradation (chains breakage). Ethanol-assisted mixing improves the thermal stability of NR/BR blends, as evidenced by the higher decomposition onset temperature and lower mass loss, especially for formula 1.

CONCLUSIONS

NR/BR blends were prepared by normal and ethanol-assisted mixing according to the three formulas. The SEM analysis showed that the additives after ethanol-assisted mixing are more evenly dispersed, thus the vulcanization performance and mechanical properties are greatly improved. The positive vulcanization time was shortened, and T_{90} decreased from 12.5 min to 10.4 min (about 17%), while the curing rate increased from 31 min^{-1} to 33 min^{-1} (6.5%). The tensile strength, elongation at break and tear strength of NR/BR blends exhibited higher values. Among them, the tensile strength of conventional formula increased from 15.4 MPa to 18.4 MPa (20%), and the dispersity decreased by 75%, from 0.08 to 0.02 MPa. The elongation at break increased from 479% to 517%, and the dispersion decreased by 50%, from 0.08 to 0.04. The aging test showed that the tensile strength of the blend obtained by normal mixing according to the conventional formula decreased by 38% (from 15.4 MPa to 9.5 MPa), while the tensile strength of the blend obtained by ethanol-assisted mixing decreased by 24% (from 18.4 MPa to 13.9 MPa), indicating excellent aging performance. Thermogravimetric analysis showed that the mass loss of NR/BR blend prepared by ethanol-assisted mixing was lower than that of normal mixing, indicating that the blend prepared by ethanol-assisted mixing exhibited better thermal stability.

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