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POLIMERY

Morphology and selected properties of NR/BR/CNT nanocomposites – effect of ethanol-assisted mixing

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Abstract: Carbon nanotubes (CNT) and ethanol-assisted mixing were used to obtain composites based on a mixture of natural rubber and butadiene rubber (NR/BR 80/20). The structure of the composites was determined by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Thermal aging tests were also carried out and the vulcanization process was characterized. SEM confirmed the homogeneous dispersion of CNTs in the polymer matrix. Improvements in tensile and tear strength as well as thermal stability were also achieved.

Keywords: natural rubber, butadiene rubber, carbon nanotubes, nanocomposites.

Struktura i wybrane właściwości nanokompozytów NR/BR/CNT – wpływ mieszania wspomaganego etanolem

Streszczenie: Do otrzymywania kompozytów na bazie mieszaniny kauczuku naturalnego i butadienowego (NR/BR 80/20) zastosowano nanorurki węglowe (CNT) i mieszanie wspomagane etanolem. Strukturę kompozytów określono za pomocą spektroskopii w podczerwieni z transformacją Fouriera (FTIR) oraz skaningowej mikroskopii elektronowej (SEM). Przeprowadzono również badania starzenia termicznego oraz scharakteryzowano proces wulkanizacji. Metodą SEM potwierdzono jednorodną dyspersję CNT w osnowie polimerowej. Uzyskano również poprawę wytrzymałości na rozciąganie i rozdzieranie oraz stabilności termicznej.

Słowa kluczowe: kauczuk naturalny, kauczuk butadienowy; nanorurki węglowe, kompozyty, dyspersja.

Natural rubber (NR) is composed of rubber hydrocarbons (polyisoprene) and contains a small amount of protein, water, resin acids, sugars, and inorganic salts. It is a nonpolar substance that is soluble in nonpolar solvents and oils. High elasticity, high constant elongation strength, excellent tear resistance and electrical insulation, good wear resistance and drought resistance, good processability, easy to adhere to other materials,

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and superior to most synthetic rubbers in terms of comprehensive performance. The disadvantages are poor oxygen and ozone resistance, poor oil and solvent resistance, and low resistance to acid and alkali corrosion [1–3]. Natural rubber is used not only to produce lightweight rubber products necessary in the household and medicine, but also to produce various rubber elements for mining, construction, electronics, aviation, as well as machine and military industries [4–7]. Rubber tires and gloves are obtained from natural rubber or rubber raw materials. The demand for natural rubber in the tire industry is over 80%, and the purchase volume of natural rubber by companies such as Linglong Tires and Sailun Tires is steadily increasing.

Cis-1,4-polybutadiene rubber (BR) is a synthetic rubber polymerized from butadiene with a cis structure content above 95% [8–10]. Various catalysts are used to obtain BR e.g., based on nickel, cobalt, titanium, and rare earth elements (neodymium). BR is the second largest synthetic rubber after styrene-butadiene rubber. Compared with natural rubber and styrene butadiene rubber, after vulcanization, its cold resistance, wear resistance and flexibility are excellent, with less heat generation under dynamic load and good aging resistance [11]. It is easy to be used together with natural rubber, neoprene, or nitrile rubber. BR is particularly suitable for the manufacture of automotive tires and cold resistant products, as well as for the manufacture of cushioning materials and rubber shoes, tapes, and sponge adhesives.

Carbon nanotubes (CNT) were discovered by predecessors of the fuller carbon system based on continuous deep exploration of carbon [12]. It is a one-dimensional quantum material with a special structure (the radial size is in the order of nanometers, the axial size is in the order of micrometers, and both ends of the tube are sealed). CNT as one-dimensional nanomaterials are lightweight, perfectly connected hexagonal structures, and have remarkable mechanical, electrical, and chemical properties. In recent years, along with the deepening of research on carbon nanotubes and nanomaterials, their wide application prospects are constantly being revealed.

There are two types of carbon nanotube nanostructures, which may be formed by spirally curling single layers of graphite, and the other is formed by curling multiple layers of graphite. Therefore, carbon nanotubes are further divided into single layer carbon nanotubes and multilayer carbon nanotubes [13]. The carbon atoms in carbon nanotubes are sp2 hybrid, while the hexagonal grid structure has a certain degree of curvature, forming a spatial topological structure. Carbon nanotubes are substances with a tubular structure, and the carbon atoms present on the inner wall have the characteristics of greater modulus and higher strength in the axial position through hybrid methods [14, 15]. Therefore, it has become a hot topic for continuous research and development [16–18].

Rubber modification methods include compounding, chemical modification, and surface modification. All these methods lead to a change in the rubber structure.

In previous work, we found that ethanol-assisted mixing can significantly improve the mechanical properties and thermal stability of rubber compounds because of better mixing of the blend components [19]. Thus, ethanol-assisted mixing can be expected to improve the dispersion of nanoparticles in the rubber matrix [20, 21].

Therefore, the article presents the effect of this kind of mixing on the carbon nanotubes dispersion in NR/BR (80/20) blend. The structure and thermal properties were analyzed by Fourier infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and thermogravimetric thermal analysis (TGA). Moreover, tensile properties, tear resistance and thermal aging, as well as vulcanization characteristic were determined.

EXPERIMENTAL PART

Materials

The natural rubber (NR, SCR5) and cis-polybutadiene rubber (BR, GB-8659-1988) were provided by Qingdao Xiangtaixing Rubber Co., Ltd. (China). Zinc oxide (ZnO), carbon nanotubes (CNT), stearic acid (SA), n-isopropyl-n′-phenyl-phenylenediamine (4010NA), n-cyclohexyl-2-benzothiazole sulfonamide (CZ), and sublimated sulfur (S) were supplied by Shandong Xilong Chemical Co., Ltd. (China).

Preparation of NR/BR/CNT composites by standard method

NR/BR/CNT composites were obtained according to a procedure published elsewhere [19]. Briefly, the rubbers

T a b l e 1. NR/BR/CNTs formulas

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

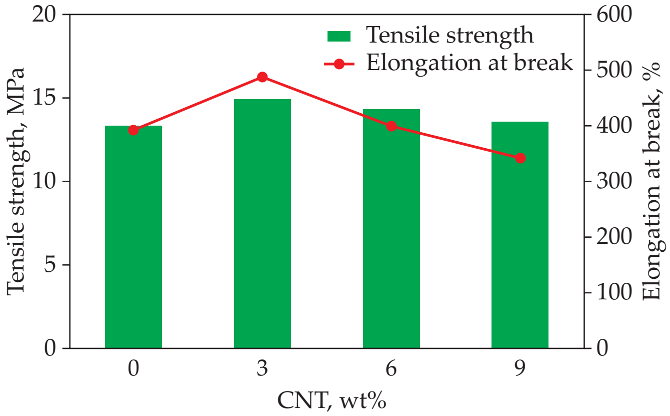

Fig. 1. Tensile properties of NR/BR 80/20 blend differing in CNT content

(NR and BR) were mixed in a specific ratio (80/20) using an open mill. The plasticizing process was carried out in an open grinder according to three formulas (Table 1). A six-fold triangular wrap was performed to ensure that the additives were evenly dispersed within the rubber matrix. The roll spacing was 1-2 mm, thin sheets were obtained after 8 times of processing.

Preparation of NR/BR/CNT composites by ethanol-assisted mixing

Additives, CNT and absolute ethanol were stirred for 15 min using a cantilever electric stirrer, dried naturally and then ground in a mill. In the next stage, the mixture of NR and BR was plasticized with powdered additives and CNTs in a two-roll mill. The process was continued as in the standard method.

Methods

Fourier transform infrared (FTIR) spectra were recorded on Zhongshi Walker Technology Development 1500 FTIR (China) spectrometer. The spectra were recorded using at least 64 scans with 4 cm^{-1}. Scanning electron microscopy (SEM) analysis was conducted using a Jeol JSM-2000EX (Japan) instrument with an acceleration voltage of 10 kV. Tensile properties and tear strength tests were determined with a universal tensile machine (DXLL-50000, Shanghai Dejie Instrument Equipment Co., Ltd., China) and a rotor free curve tester (MDR2000, Shanghai Dejie Instrument Equipment Co., Ltd, China) according to GB/T528 and GB/T529, respectively. The crosslinking reaction was investigated with flat vulcanizer (25 tons QLB 350×350×2, Shanghai Rubber Machinery Factory, China) according to GB/T16584. Aging tests were performed at 60°C for 120 h using a jet dryer (101-3A, Tianjin Taist Instrument Co., Ltd, China). The thermal stability was determined by TGA measurements (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.

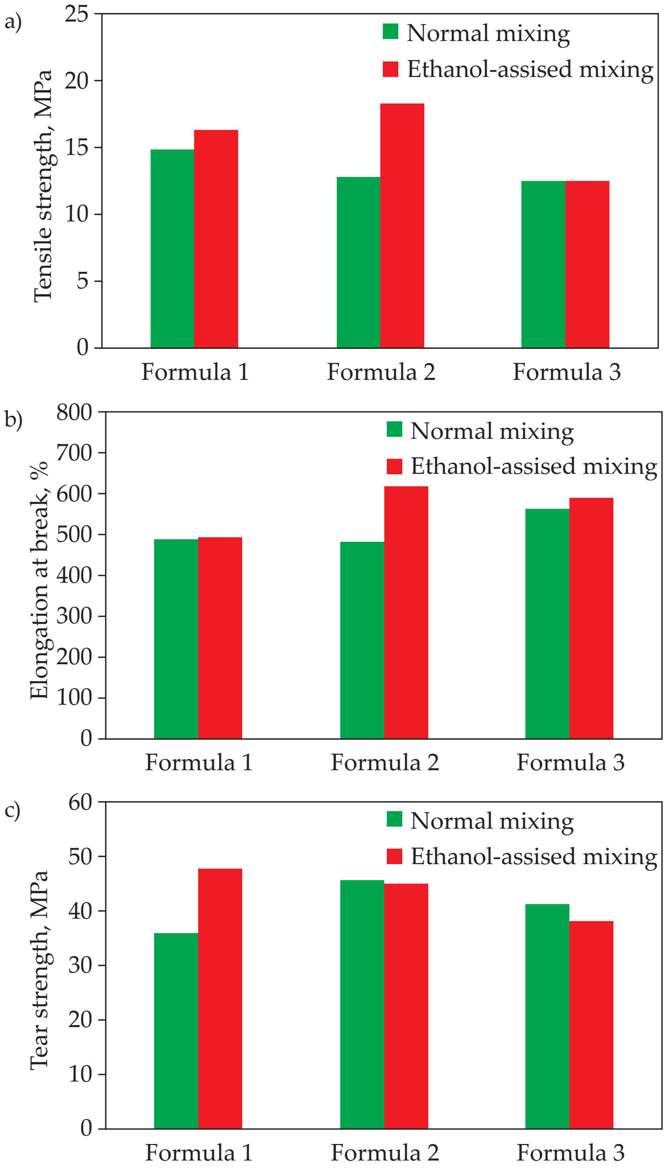

Fig. 2. Mechanical properties of NR/BR/CNTs composites: a) tensile strength, b)elongation at break, c) tear strength

RESULTS AND DISCUSSION

Mechanical properties

As shown in Fig. 1, the tensile strength and elongation at break of the NR/BR 80/20 blend prepared according to conventional formula were significantly increased by adding 3 wt% CNT. Besides, such a composite showed higher strength and elongation than composites with a higher CNT content (6 and 9 wt%). Therefore, a composite containing 3 wt% CNT was selected for further research.

Figure 2 shows the mechanical properties of NR/BR/CNT composites prepared according to three different formulations. The addition of CNT significantly improved the mechanical properties of the NR/BR blend, with better properties obtained using the ethanol-assisted mixing method. It is well known that CNT have extremely high modulus and tensile strength and large

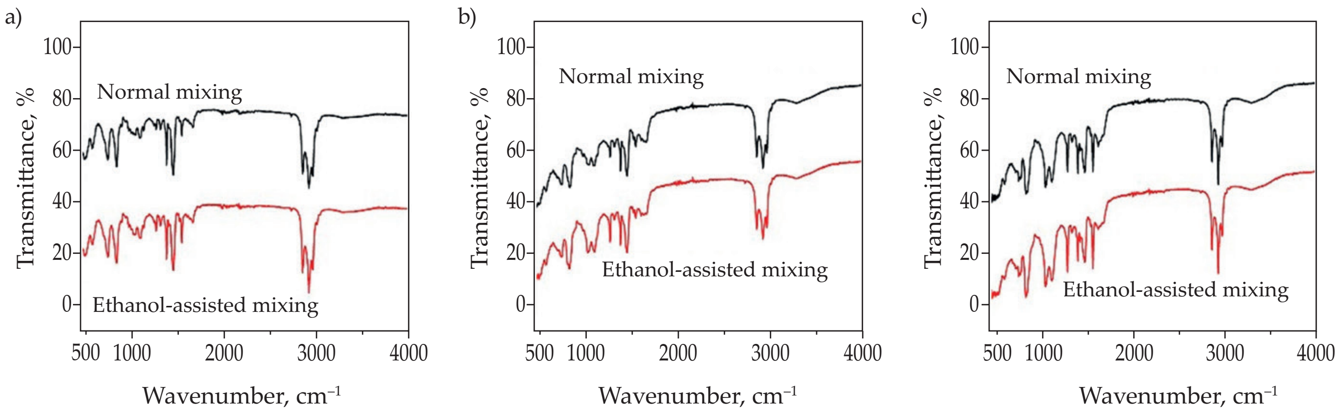

Fig. 3. IR spectra of NR/BR/CNTs composites: a) formula 1, b) formula 2, c) formula 3

aspect ratio, and when added to rubber, they will interact with rubber particles, limiting the fracture of rubber molecular chains, significantly improving mechanical and barrier properties of rubber composites [22, 23]. At the same time, after wet modification, the crosslinking degree between the filler and rubber is higher, and the activity of CNT is higher, and the binding degree with rubber molecules is better, making the nanocomposites modified by ethanol-assisted mixing method more uniform [19].

IR analysis

FTIR spectra of NR/BR/CNT composites are shown in Fig. 3. Compared to normal mixing, the ethanol-assisted mixing showed a higher intensity of C-O phenol stret-

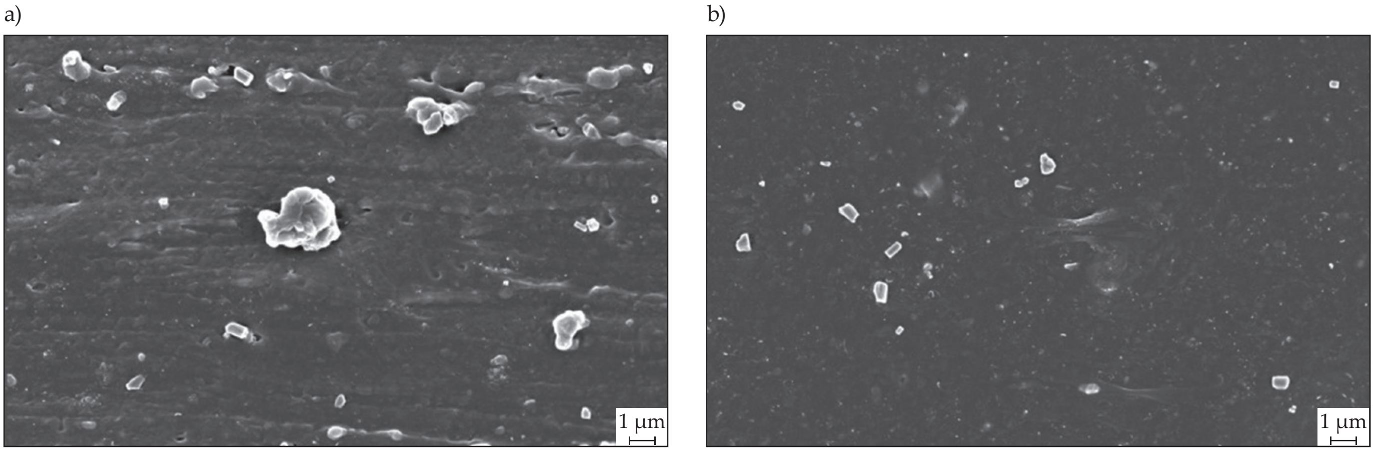

Fig. 4. SEM images of NR/BR/CNT composites obtained using conventional formula: a) normal mixing, b) ethanol-assisted mixing

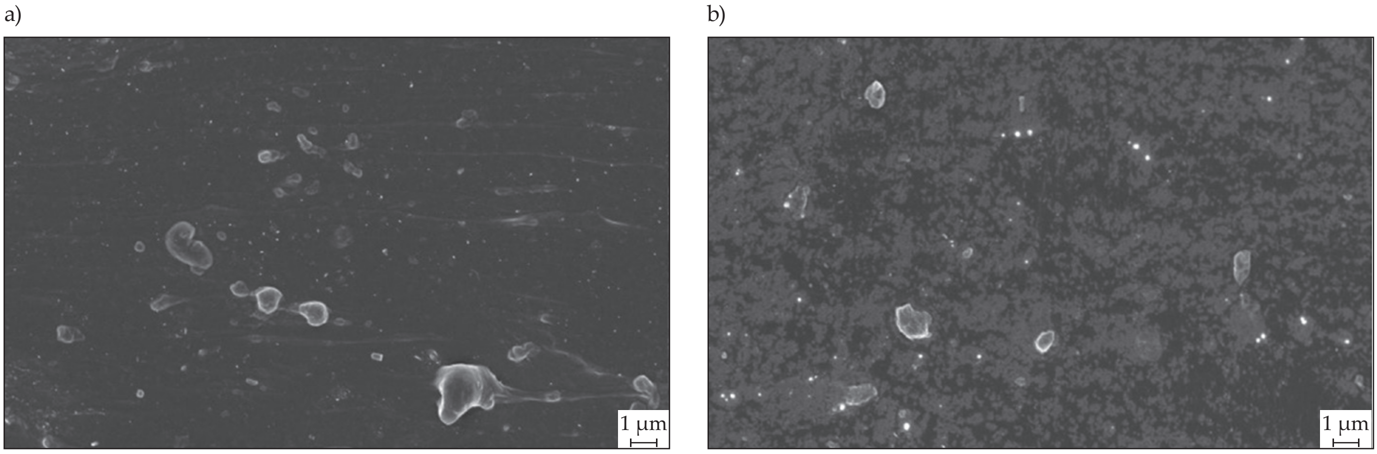

Fig. 5. SEM images of NR/BR/CNT composites obtained using high sulfur formula: a) normal mixing, b) ethanol-assisted mixing

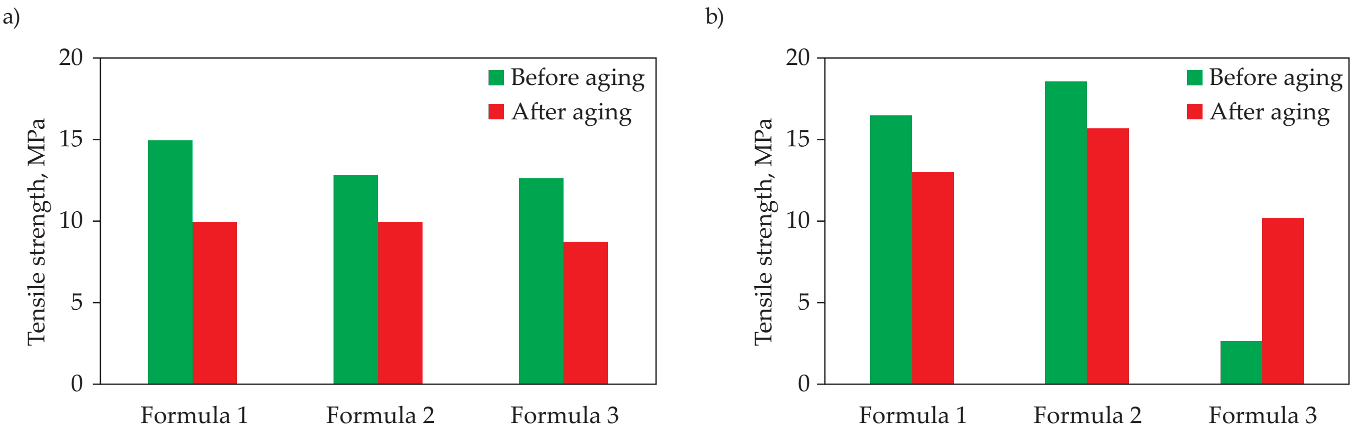

Fig. 6. Effect of thermal aging on mechanical properties of nanocomposites: a) normal mixing, b) ethanol-assisted mixing

ching vibrations at 1013 cm^{-1} for the composite prepared in the high-sulfur formula and a higher intensity of C-S bond stretching vibrations at 800 cm^{-1} and tertiary amine C-N bond stretching vibrations at 1260 cm^{-1} for the composite prepared in the low sulfur formula. Ethanol-assisted mixing increases the compatibility between the filler and the rubber, while promoting the conversion of active groups in the filler, so it bonds better with the rubber, as evidenced by the higher intensity of the infrared peaks, resulting in a more uniform dispersion of the filler in the NR/BR matrix and its better activity.

SEM analysis

In this study, SEM was used to investigate the dispersion of CNT and other fillers in NR/BR blend. Figures 4

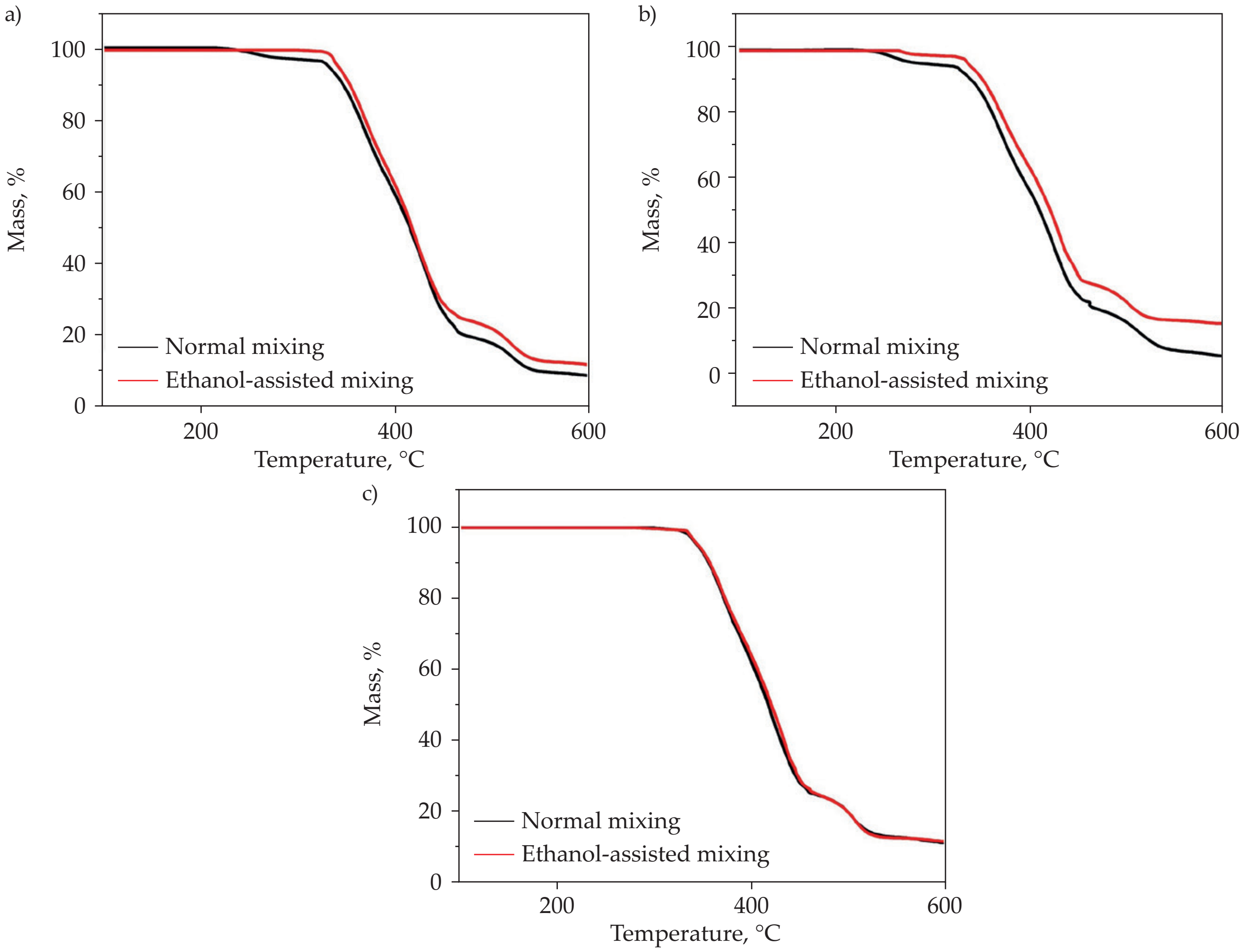

Fig. 7. TGA curves of NR/BR/CNT composites: a) formula 1, b) formula 2, c) formula 3

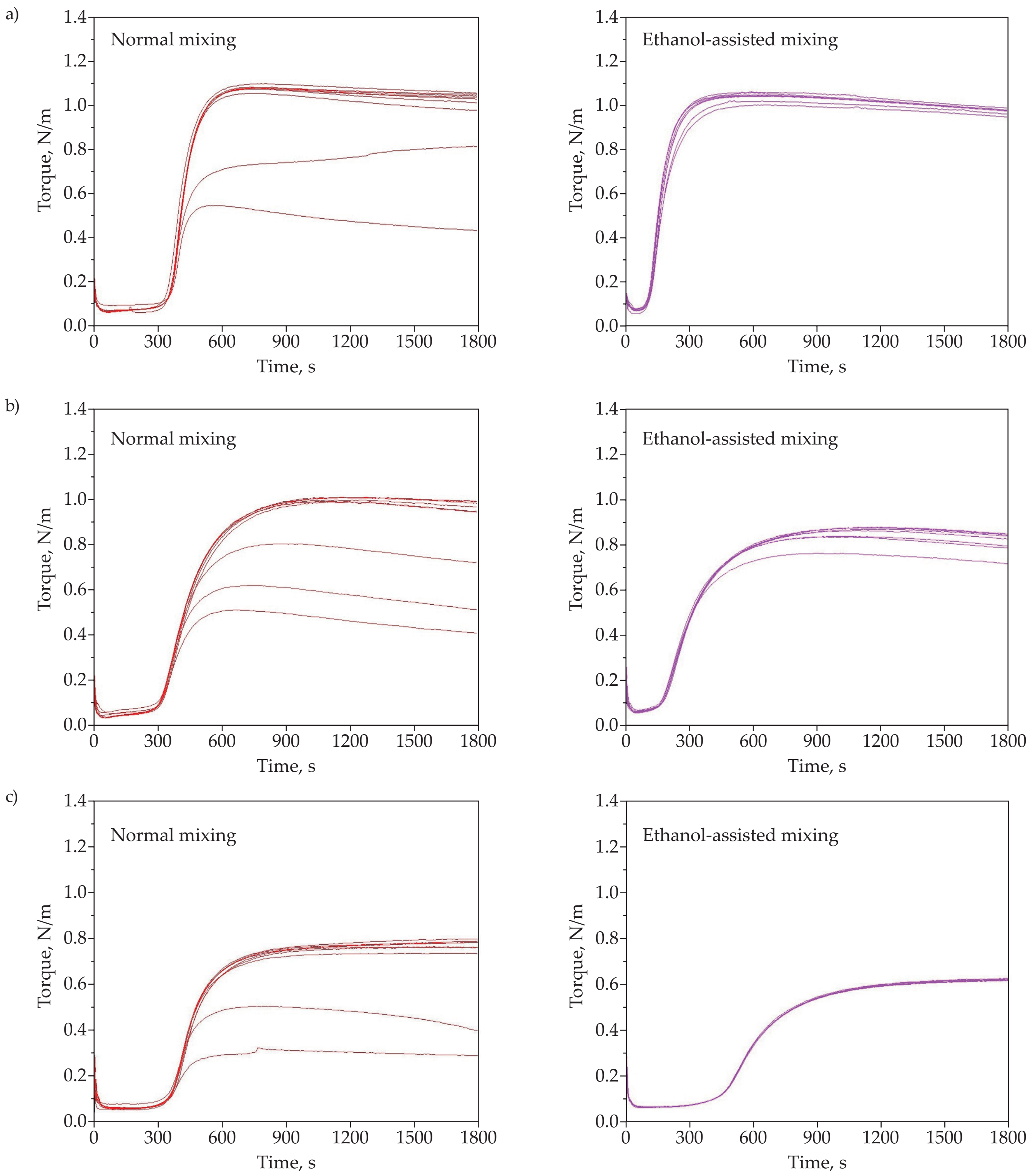

Fig. 8. Curing curves of NR/BR/CNT composites: a) formula 1, b) formula 2, c) formula 3

and 5 show SEM images of NR/BR/CNT composites obtained according to conventional and high sulfur formulas, respectively. The black part is the rubber matrix, and the white parts are CNT and other fillers. It is evident that CNT particles are homogeneously dispersed in the composites. However, composites obtained by ethanol-assisted mixing, regardless of the formula used, were characterized by better compatibility than those obtained by normal mixing.

Thermal aging

Figure 6 shows tensile strength before and after thermal aging of NR/BR/CNT composites obtained by normal mixing and ethanol-assisted mixing using three different formulas. After thermal aging, the tensile strength of the composite obtained according to conventional formula (formula 1) by normal mixing decreased by 33%, and that of the composite obtained by mixing with ethanol by 21%. On the other hand, the tensile strength of the composite obtained according to formula 2 and the normal mixing method decreased by 23%, while the tensile strength of the composite obtained using ethanol-assisted mixing decreased by 15%. In the case of formula 3, the tensile strength of the composite prepared by normal mixing decreased by 31%, while that of the composite prepared using ethanol-assisted mixing by 20%. Ethanol-assisted mixing results in a more uniform dispersion of fillers in the rubber matrix, as confirmed by SEM (Figs. 4, 5). In addition, ethanol-assisted mixing can increase the antioxidant activity, thereby improving the aging resistance of the rubber. It can be concluded that the NR/BR/CNT composites obtained in the ethanol mixing process are characterized by a higher resistance to thermal aging compared to those obtained because of normal mixing.

Thermogravimetric analysis

Figure 7 shows the thermogravimetric curves of NR/BR/CNT composites. In the case of ethanol-assisted mixing, the thermal decomposition onset temperature of the composites increased compared to normal mixing, while the rate of thermal degradation decreased. At the same time, the mass loss at the same temperature was lower than with normal mixing. Carbon nanotubes can prevent the formation of free radicals during the thermal degradation of rubber. However, the small number of free radicals generated will combine with CNT to form stable free radicals. In the case of ethanol-assisted mixing, the activity of CNT is stronger, and they can bind better to generated free radicals, which results in a lower rate of thermal degradation.

The addition of CNT increases the thermal degradation temperature and reduces the thermal decomposition rate of NR/BR/CNT composites. The mass loss of the composites obtained by ethanol-assisted mixing is lower than that of normal mixing. The ethanol-assisted mixing improved the thermal stability of NR/BR/CNT composites.

Vulcanization characteristics

Figure 8 shows the vulcanization curves of composites obtained by normal mixing and ethanol-assisted mixing. The difference between the maximum and minimum torque of vulcanizates prepared by mixing with the addition of ethanol is much smaller than in the case of normal mixing. The maximum torque decreases and the minimum torque increases, the values depending on the formula used. In the case of formula 3, the vulcanization curves practically coincide. In addition, the use of ethanol mixing reduces scorch time and vulcanization time compared to mixing without ethanol. Ethanol-assisted mixing is believed to increase the compatibility of CNT with rubber, resulting in their uniform dispersion in the rubber matrix and improved mechanical properties. The difference between the maximum and minimum torque is also smaller and the vulcanization time is shorter. The beneficial effect of ethanol-assisted mixing on the vulcanization process of the NR/BR blend was confirmed by the authors' earlier research [19].

CONCLUSIONS

SEM showed that NR/BR/CNT composites were successfully prepared using ethanol-assisted mixing. The composites obtained in this way were characterized by good compatibility, which resulted in better mechanical and thermal properties as well as resistance to thermal aging. Moreover, the vulcanization characteristics indicated a reduction in the positive vulcanization time of the composites obtained by ethanol-assisted mixing, a decrease in the maximum torque, and a significant increase in the speed of vulcanization.

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