Research Article

Carbon black reinforced natural rubber/butadiene rubber and natural rubber/butadiene rubber/styrene-butadiene rubber composites: Part II. Dynamic mechanical properties and fatigue behavior

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Article Info	Abstract
	Carbon black reinforced natural rubber (NR)/butadiene rubber (BR), NR/styrene-butadiene rubber (SBR) and NR/BR/SBR composites were prepared by using two types of BR with highly linear chain structure (higher viscosity and molecular weight) and branched chain structure (lower viscosity and molecular weight). NR/BR composite consisting of BR with higher viscosity has the highest fatigue strength. Damping factors of NR, NR/SBR and NR/BR/SBR composites as a function of frequency were systematically compared at constant temperatures of -40, 0, 25 and 60°C. Based on dynamic mechanical analysis (DMA) results, the elasticity of NR/carbon black composite improves, its heat buildup character and tan δ decreases with the addition of BR. The addition of 20 phr BR to NR/SBR composites provides 4-5 times better fatigue strength due to the decrease of tan δ. Lastly, using a higher viscosity BR in carbon black filled NR or NR/SBR is quite favorable in terms of using these composites as anti-vibrational rubber bushings in automotive applications where high fatigue resistance and lower damping factor are important criteria.

1. Introduction

The dynamic mechanical properties and fatigue behavior of rubber composites have important roles in predicting the service life of final products in automotive industry. Especially, some parts of the framework in trucks cannot be changed easily in periodic maintenance, and it means high maintenance costs. Also, the long fatigue life and better damping properties of rubber products can provide better driving dynamics, safety and reliability. Many reasons can affect dynamic mechanical properties and fatigue life of rubber composites such as the types and amounts of fillers, main polymer, anti-degradation chemicals, other special chemicals and environmental conditions [1-4].

Natural rubber has exceptionally remarkable properties such as outstanding tensile and tear strength and good abrasion resistance which are eligible for production of O-rings, tires, conveyor belts, fluid transfer systems, body sealing systems, transmission systems, automotive antivibration, sealants, adhesives & coatings, molded parts, body parts, spare

parts etc. [5,6]. NR has a great strength in terms of fatigue behavior when it is compared with other rubbers. The strain-induced crystallization in NR increases mechanical properties especially under high amplitudes of strain. In addition, this property provides a longer fatigue life to NR in comparison with other rubbers. So, this behavior makes the natural rubber a unique elastomer in rubber industry [7-11]. The mechanism of fatigue behavior such as the nucleation and growth of defects or cracks in NR has been investigated by several researchers [1-4,10-19]. Mars *et al.* investigated the multiaxial stress effects on fatigue crack nucleation and growth in filled NR systems. The initial and additional softenings in the system were believed to be conclusions of irreversible breakage of various bonds and network chain breakage by the effect of fillers, respectively [11]. The cavitation as a result of decohesion between zinc oxides and rubber matrix was found out to be the crucial fatigue damage, and the crack tip consists of stretched elliptical regions that are surrounded by highly stretched and crystallized ligaments [13]. The cracks initiate from rigid inclusions such as SiO_2 or $CaCO_3$ particles, and large carbon black agglomerates with an average size of 200 μm that are present in natural rubber. In addition, the crack orientation is dependent on the type and maximum level of loading [14].

Styrene-butadiene rubber has been used in NR blends since it has better abrasion resistance, crack initiation resistance, high filler-loading capacity and lower heat-build up behavior [5,6,20,21]. SBR is generally used in wear applications. SBR is usually blended with NR in order to improve its tensile and tear properties [5,6,21]. Thus, SBR has been used in a wide range of products such as side walls of tires, belts, hoses, foot wears, foamed products, etc. [5,6].   Mechanical, thermomechanical, fatigue and rheological properties of NR/SBR composites have been studied by several researchers [5,6,20,21]. Based on dynamic mechanical and mechanical results of NR/SBR composites, it was revealed that the storage modulus decreases and loss modulus and tan δ increase with increasing temperature and NR concentration [20]. Based on DMA results, it was previously shown that SBR/NR blends are incompatible due to their two distinct glass-transition temperatures [20,21].

It is well-known that unfilled or unreinforced rubber has a low modulus, poor abrasion resistance and fatigue behavior [3,4,22]. Carbon blacks are generally used to improve the mechanical behavior of rubber. However, this reinforcing method is not sufficient by itself especially in the fabrication of heavy industrial rubber products. Rubber composites that have close elastic modulus exhibit similar mechanical properties. But in terms of fatigue behavior and service life, changes in the types of polymers lead to quite different fatigue resistance [3,4]. A longer fatigue life can be achieved in rubber composites by using butadiene rubber in the matrix [3,4,23]. BR increases chain flexibility at lower temperatures, filler loading capacity, and decreases heat-build up and energy consumption during mastication [1,3,4,24]. Thus, blending different types of natural rubber composite with BR is a typical method to improve the fatigue life [3,4,23,24]. It was previously shown that the abrasion resistance, rebound resilience and hardness of natural rubber increases, however its glass transition temperature decreases with the addition of butadiene rubber [23]. Furthermore, better mechanical properties in NR/BR composites were obtained by using carbon blacks that can be well dispersed in the rubber matrix [23]. In addition to a few number of carbon black containing NR/BR composite studies in the literature, recent works in this area have been focused on the use of nano and micron-sized fillers in NR/BR/carbon black composites.

Among nano-sized filler containing NR/BR/carbon black composite studies in the literature, the use of carbon nanotubes [25,26], halloysite nanotube [27], nanoclay [27,28] and nano zinc oxide [29] in NR/BR/carbon black composite matrix can

be given as examples. In addition, micron-sized silica [24,29], and organomodified kaolin [24,30] were used in NR/BR/carbon black composites to enhance the curing characteristics, fatigue resistance, mechanical and dynamic mechanical properties.

The dynamic mechanical properties of NR/BR and SBR/BR composites were improved with the addition of suitable amounts of ultrafine full-vulcanized styrene-butadiene powdered rubber [31]. Tension and compression tests of SBR/BR/NR composites revealed that changes in frequency, strain rate and load do not significantly influence the fatigue life. However, if the values of frequency and maxiumum strain are higher, the values of sample temperature and thermal load are higher due to the hysteresis of rubber composites [16].

In this paper, carbon black reinforced NR/BR, NR/SBR and NR/BR/SBR composites were prepared by using two types of BR with highly linear chain structure (higher molecular weight and viscosity) and branched chain structure (lower viscosity and molecular weight). The composition of rubber matrices was varied while the proportions of other components (carbon black and small chemicals) were held constant. The purpose of this work is to investigate and compare dynamic mechanical properties and fatigue life of carbon black filled NR/BR, NR/SBR and NR/BR/SBR composites. The focus of this work is to show that carbon black reinforced NR/BR and NR/BR/SBR composites containing two types of BR with different chain structures, viscosities and molecular weights display significant property improvements in terms of fatigue life and dynamic mechanical properties compared to carbon black reinforced NR and NR/SBR composites, respectively. Previous studies of carbon black filled NR/BR and NR/BR/SBR composites and NR/BR/carbon black composites consisting of nano and micron-sized fillers have been investigated by several researchers in the literature. However, to the best of our knowledge, no systematic work has been reported about the effect of using two types of BR with different molecular weights and viscosities on the fatigue life and dynamic mechanical properties of carbon black reinforced NR/BR and NR/BR/SBR composites.

2. Experimental

2.1 Materials

Natural rubber that was used in this study is standard Vietnam rubber constant viscosity 60 (SVR CV60) since this grade can maintain its viscosity during and after mastication. For butadiene rubber, cis-Polybutadiene Nd Catalyst was preferred which is widely used in rubber industry. There are two different BR grades in terms of Mooney viscosity in the market which belongs to LANXESS, and they are named as Buna CB 22 (BR1) and CB 24 (BR2). They have 63 and 44 Mooney viscosity, respectively. BR1 has a relatively higher linear chain structure, molecular weight and viscosity compared to BR2. For styrene butadiene rubber, SBR 1502 which has high filler capacity, low heat-build up character and 55±3 Mooney viscosity was used in NR composites. The glass transition temperatures of NR, SBR, butadiene rubber (both BR1 and BR2) are -70°C, -58°C and -92°C, respectively. The composition of NR composites is given in Table 1.

N330 (High Abrasion Furnace) carbon black was used as a filler material in the same amount in all NR composites. In NR composites, the composition of rubber matrices was varied while the proportions of other components (carbon black and small chemicals) were held constant. The chemical composition of the reference sample NR composite is given in Table 2.

Table 1 The composition of NR composites (BR1: Buna CB22, BR2: Buna CB24)

Sample Composition	NR (phr)	SBR (phr)	BR1 (phr)	BR2 (phr)
NR	100	-	-	-
NR/SBR	50	50	-	-
NR/BR1	50	-	50	-
NR/BR1/SBR	50	30	20	-
NR/BR2	50	-	-	50
NR/BR2/SBR	50	30	-	20

Table 2   The chemical composition of the reference composite (NR)

Constituent	Amount (phr)
SVR CV 60 (NR)	100
Carbon Black N330 (Filler)	50
Zinc Oxide (ZnO)	5
Stearic Acid (StA)	1.5
Aromatic Oil	3
Protective Agents	4
Sulphur (S-80)	3
Total	166.5

2.2 Fabrication of carbon black filled rubber composites

All samples were mixed in an open laboratory mill that has two rolls. The masterbatch, sulphur powder and final batch are shown in Fig.1. Firstly, carbon black, and then small chemicals were added to the rubber matrix. All samples were mixed in the lab mill at about the same time. During the mastication process, the temperature of rolls was controlled periodically to prevent any uncontrolled temperature increase. The final batch before and during mixing with sulphur powder and accelerators on a two-roll mill are shown in Figs. 2(a) and (b), respectively.

(a)

(b)
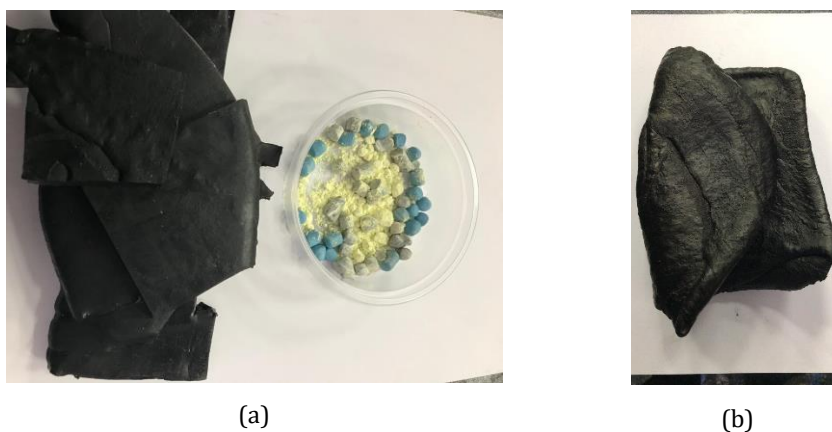
Fig. 1(a) The masterbatch, sulphur powder and accelerators (b) The final batch

(a)   (b)

Fig. 2(a) The final batch before mixing with sulphur powder and accelerators on a two-roll mill and (b) the final batch during mixing with with sulphur powder and accelerators on a two-roll mill

2.3 Physical/Chemical Characterization

2.3.1. Dynamic mechanical analysis (DMA)

The damping behavior of NR composites was analyzed by using a MetraVib +1000 dynamic mechanical analysis (DMA) instrument. DMA tests of cylindrical NR vulcanizates were carried out by using the compression mode with frequency sweep from 1 Hz to 200 Hz at constant temperature. The temperatures were chosen as −40°C, 0°C, 25°C and 60°C. Cold temperatures were achieved by pumping liquid nitrogen to the sample compartment from liquid nitrogen tank that is attached to the DMA instrument. Also, hot temperatures were obtained by using the heater inside DMA. The DMA compression mode samples which were prepared from the compression set mold have a diameter of 12 mm and a thickness of 6.30 mm. There is no specific standard for sample dimensions in the compression mode of DMA. All the samples have the same dimensions to obtain good consistent data. In addition, the experimental procedure for the DMA compression tests were also executed in the same manner for all the samples. For each sample, three repetitions were made to obtain consistent data. The parameters such as storage and loss moduli and tan δ were automatically obtained or calculated by the software that is running the DMA instrument.

2.3.2. Fatigue analysis

The fatigue behavior of NR composites was determined by using Alpha Fatigue to Failure Tester (FTFT) with only one constant 1.78 extension ratio, 1.67 Hz and tensile load according to ASTM D4482. All the samples were subjected to same experimental conditions. In FTFT experiment, 1.78 extension ratio corresponds to % 78 strain value in a typical static stress-strain experiment. And this value is about %322 lower compared to the maximum elongation of NR sample in this study. For each sample, maximum strain was %78 and minimum strain was %0 during each cycle. For each NR vulcanizate, six samples were tested and averaged to determine the fatigue behavior. In the FTFT test, the criteria of fatigue damage is defined as complete rupture of test specimen according to ASTM

D4482. So, the number of cycles to failure (fatigue life) was recorded up to the complete material breakage for each sample. The dumbbell shaped specimens have a gauge length of 25 mm, a thickness of 2 mm and a width of 4 mm. The pictures of a fatigue sample and FTFT are given in Fig.3.
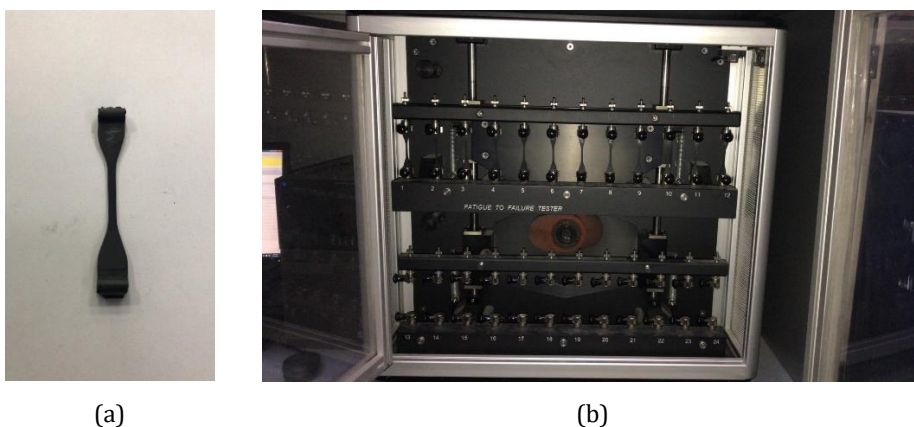

(a)   (b)

Fig. 3(a) The FTFT test sample and (b) the Alpha Fatigue to Failure Tester (FTFT)

2.3.3. Scanning electron microscopy (SEM)

SEM experiments were performed by using a JEOL JSM 7001F. The SE detector, HV mode, 15.00 and 10.00 kV accelerating voltages were used during the experiments. Samples were coated with 5-6 nm Au-Pd to induce electrical conductivity. The SEM images were taken from sample surfaces which were fractured after the samples were subjected to static stress-strain tests. NR sample was ruptured at a tensile stress of 18 MPa and a maximum elongation of % 400. In addition, NR/BR1 sample was ruptured at a tensile stress of 16 MPa and a maximum elongation of % 410.

3. Results and Discussion

DMA results of NR composites at -40°C, 0°C, 25°C and 60°C are given in Figs.4-7, respectively. At all temperatures, the elasticity of NR matrix improves since carbon black particles are relatively well-dispersed with the addition of butadiene rubber. Thus, tan δ decreases, and the heat buildup character or loss modulus of NR/BR composite system also diminishes. As can be seen from Figs.4-7, the butadiene rubber gives more chain flexibility to the composite especially at lower temperatures due to the highly linear chain structure and relatively lower T_g of BR.

In Fig.4, at -40°C, NR/SBR has the highest tan δ since it is the most rigid composite because of its 23% styrene content. In Fig.4, at -40°C, NR/BR2 composite exhibits a higher tan δ compared to NR/BR1 since the storage modulus of NR/BR1 composite is relatively much higher compared to NR/BR2 due to the higher viscosity of BR1. Also, in agreement with previous Payne effect and dispergrader results [32], the loss modulus of NR/BR2 composite is much higher compared to that of NR/BR1 since filler-filler interactions are much higher in NR/BR2 compared to NR/BR1 composite. In Fig.4, NR/BR1/SBR composite displays a higher tan δ compared to NR/BR2/SBR since filler-filler interactions increase due to the higher viscosity of BR1. The increase of filler-filler interactions in NR/BR1/SBR composite compared to NR/BR2/SBR is also confirmed by Payne effect results from our previous work [32]. Thus, this behavior leads to higher loss modulus and tan δ in NR/BR1/SBR in comparison with that of NR/BR2/SBR composite.
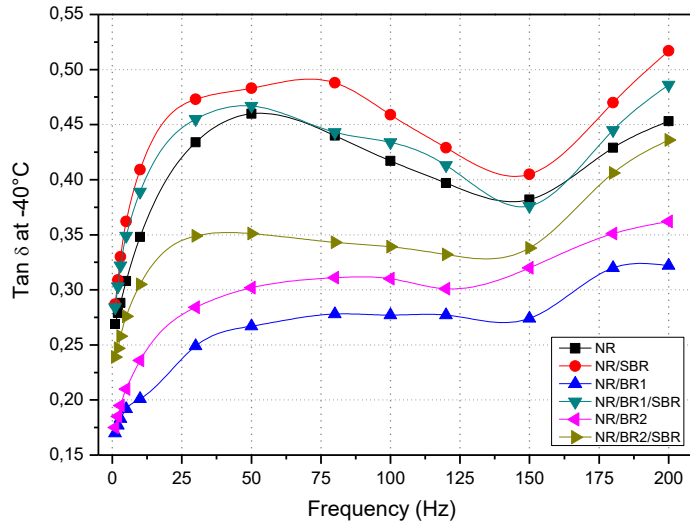
Fig. 4. DMA results of NR, NR/BR, NR/SBR and NR/BR/SBR composites at -40°C.

In Fig.5, at 0°C, due to the increase of temperature, tan δ of NR/SBR decreases slightly at all frequencies compared to that at -40°C, and its profile almost becomes equal to that of NR composite. As the temperature increases from -40°C to 0°C, tan δ of NR/BR2 decreases more than that of NR/BR1, and tan δ profiles of NR/BR1 and NR/BR2 almost become equal at all frequencies. In Fig.5, NR/BR1/SBR composite displays a higher tan δ compared to NR/BR2/SBR since filler-filler interactions increase due to the higher viscosity of BR1.
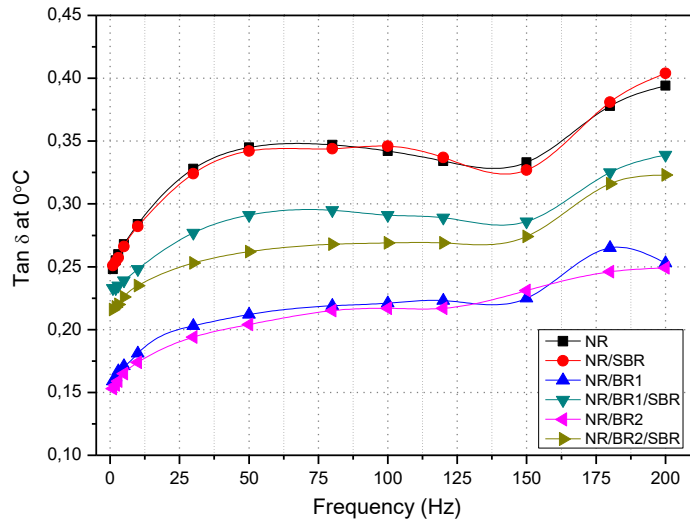

Fig. 5. DMA results of NR, NR/BR, NR/SBR and NR/BR/SBR composites at 0°C.
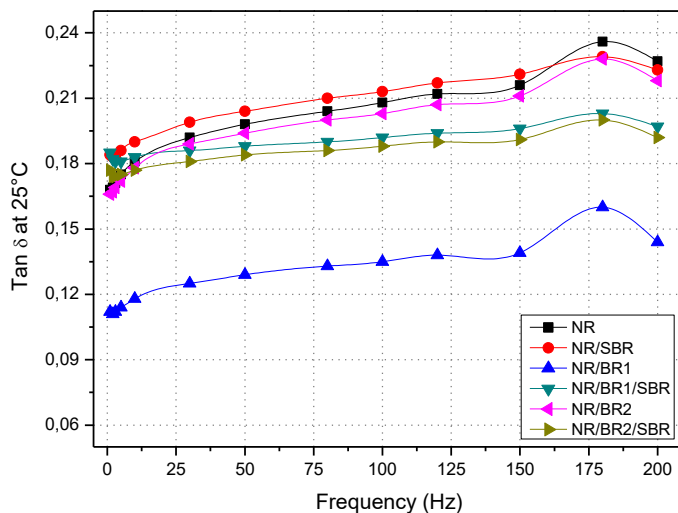
Fig. 6. DMA results of NR, NR/BR, NR/SBR and NR/BR/SBR composites at 25°C.

In Fig.6, at 25°C, due to the increase of temperature from 0 to 25°C, tan δ profiles of NR/SBR and NR decrease slightly at all frequencies compared to those at 0°C, and their tan δ values profiles are almost equal to each other. As the temperature increases from 0°C to 25°C, tan δ of NR/BR1 decreases more than that of NR/BR2, and tan δ profile of NR/BR2 becomes much higher than that of NR/BR1 at 25°C. At this temperature, storage and loss modulus values of both NR/BR1 and NR/BR2 decrease compared to the case at 0°C. But, the decrease in storage modulus in NR/BR2 is more pronounced compared to NR/BR1 due to the higher viscosity of BR1. Thus, the storage modulus of NR/BR1 is much higher and its tan δ is much lower compared to NR/BR2 at all frequencies. In Fig.6, at 25°C, NR/BR1/SBR composite displays a higher tan δ compared to NR/BR2/SBR since filler-filler interactions increase due to the higher viscosity of BR1. The increase of filler-filler interactions in NR/BR1/SBR composite compared to NR/BR2/SBR is also confirmed by Payne effect results from our previous work [32]. Thus, this behavior leads to higher loss modulus and tan δ in NR/BR1/SBR in comparison with that of NR/BR2/SBR composite.

In Fig.7, at 60°C, tan δ of NR/SBR composite is much lower compared to NR due to the higher T_g and high filler loading capacity of SBR. As the temperature increases from 25°C to 60°C, tan δ of NR/BR2 decreases more than that of NR/BR1, and tan δ profile of NR/BR1 becomes much higher than that of NR/BR2 at 60°C. In Fig.7, at 60°C, NR/BR1/SBR composite displays a higher tan δ compared to NR/BR2/SBR since filler-filler interactions increase due to the higher viscosity of BR1. As the temperature increases from 25°C to 60°C, tan δ of NR/BR2/SBR decreases, and tan δ profile of NR/BR2/SBR becomes much lower than that of NR/BR1/SBR. Storage and loss modulus values of NR/BR2/SBR decrease compared to the case at 25°C. But, the decrease of loss modulus in NR/BR2/SBR is more pronounced than the decrease of storage modulus. In the case of NR/BR1/SBR composite, as the temperature increases from 25°C to 60°C, tan δ of NR/BR1/SBR does not change that much at all frequencies.
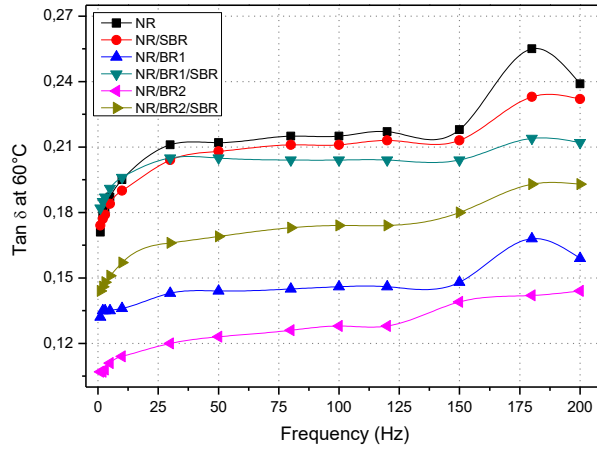
Fig. 7. DMA results of NR, NR/BR, NR/SBR and NR/BR/SBR composites at 60°C.

Fatigue results are given in Fig. 8. As can be seen from FTFT results, the most durable composite is NR/BR1, and it has 1.5 million of cycles in terms of fatigue failure. This is because the presence of BR component which has a higher linear chain structure, molecular weight and viscosity improves elasticity and storage modulus. Fatigue behavior is directly related with the elastic characteristics of sulphur bonds which are located between polymer chains [33-35]. Single bridges of sulphur (monosulphidic bridges) are known as more elastic and reliable in terms of chemical bonding [33,35]. Monosulphidic bridges propagate relatively more less in comparison with polysulphidic bridges, and this behavior leads to optimal thermomechanical properties (less relaxation in stress and less compression set) but lower fatigue resistance [33,35]. In addition, broken monosulphidic bonds have less possibility in terms of bonding again spontaneously in contrast to polysulphidic bonds [33,35]. However, the vulcanization system that was used in the NR/BR1 composite consists of both mono and polysulphidic bonds. So, for this reason, this vulcanization system provides more elasticity, superior thermomechanical properties [32] and higher fatigue resistance at the same time.
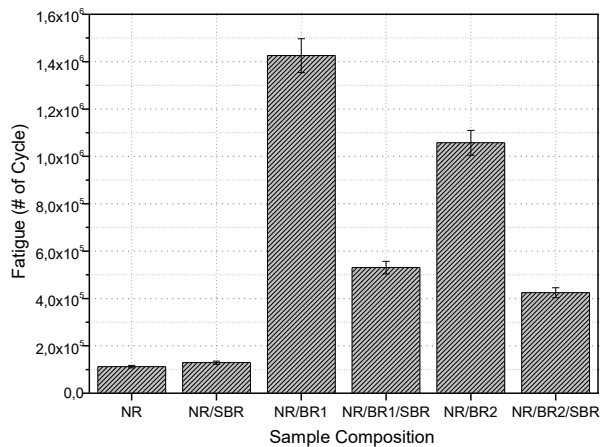

Fig. 8. Fatigue results of NR, NR/BR, NR/SBR and NR/BR/SBR composites.

Fatigue behavior deteriorates with increasing tan δ of NR composites. For instance, in comparison with NR/BR1, the fatigue resistance of NR/BR1/SBR composite is much lower due to the addition of 30 phr addition of SBR instead of BR1. In comparison with NR/SBR composite, fatigue strengths of NR/BR1/SBR and NR/BR2/SBR composites exhibit higher values. Here, the composition of NR/SBR composite is 50/50 phr. Thus, compared to NR/SBR, in NR/BR/SBR composites, taking out 20 phr SBR and adding 20 phr BR provide 4-5 times better fatigue strength values due to the decrease of tan δ.
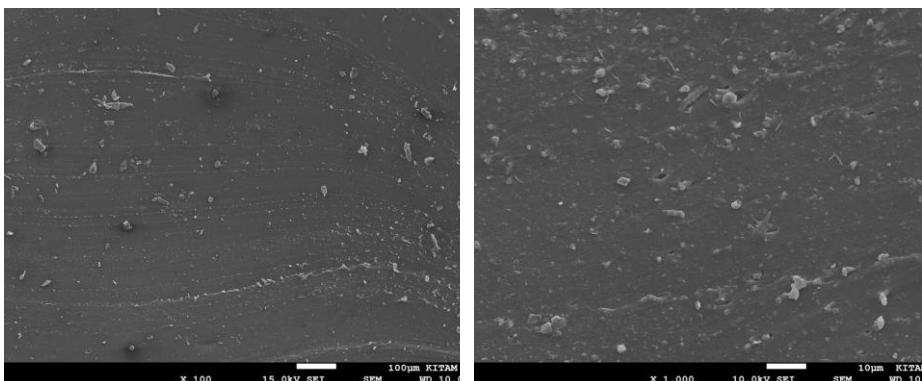

Fig. 9. SEM micrographs of NR composite.

SEM images of fracture surfaces that belong to carbon black reinforced NR and NR/BR1 composites are shown in Figures 9 and 10, respectively. In Fig.9, it is clearly seen that carbon black reinforced NR composite that does not contain any BR component has a relatively sharp and brittle fracture surface. In NR composite, filler-filler interactions were observed to be higher due to the absence of BR based on damping, fatigue and previously observed Payne effect results [32].
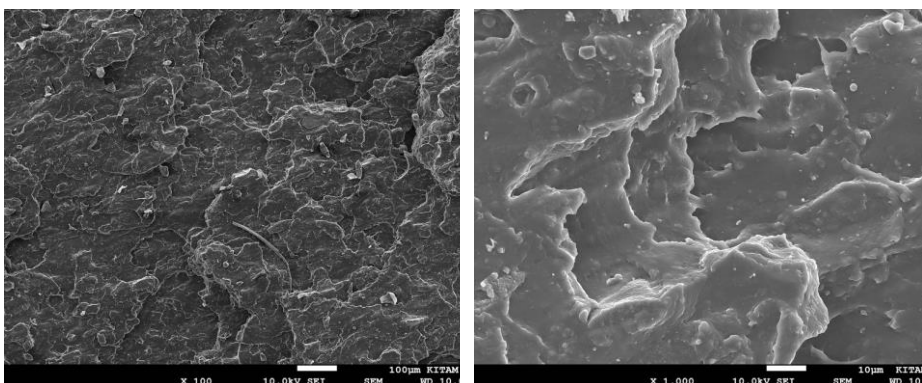

Fig. 10.   SEM micrographs of NR/BR1 composite

In Fig.10, in NR/BR1 composite, since BR gives more elasticity to NR blends, the fracture process appears more ductile, and the crack propagation becomes more difficult compared to NR composite. Thus, for this reason, the fatigue life of NR/BR1 is much higher compared to NR composite since a crack needs more energy to propagate in a softer matrix with a higher ductile property.

4. Conclusion

In summary, carbon black reinforced NR/BR, NR/SBR and NR/BR/SBR composites were prepared by using two types of BR with highly linear chain structure (higher viscosity and molecular weight) and branched chain structure (lower viscosity and molecular weight). Dynamic mechanical properties and fatigue life of carbon black filled NR/BR, NR/SBR and NR/BR/SBR composites were systematically compared with each other. Based on DMA results, at all temperatures, the elasticity of NR matrix improves since carbon black particles are relatively well-dispersed with the addition of butadiene rubber. Thus, tan δ decreases, and the heat buildup character of NR/BR composite system also diminishes. Especially at lower temperatures, the butadiene rubber gives more chain flexibility to the rubber composite due to the linear chain structure and relatively lower T_g of BR. In addition, at all temperatures, NR/BR1/SBR composite displays a higher tan δ compared to NR/BR2/SBR since filler-filler interactions increase due to the higher viscosity of BR1 compared to BR2. Fatigue results clearly show that the most durable composite is NR/BR1, and it has 1.5 million of cycles in terms of fatigue failure. This is because the presence of BR component with a higher molecular weight and viscosity in NR improves elasticity and storage modulus. Fatigue behavior deteriorates with increasing tan δ of blends. For instance, in comparison with NR/BR1 composite, the fatigue resistance of NR/BR1/SBR is much lower due to the addition of 30 phr addition of SBR instead of BR1. The addition of 20 phr BR to NR/SBR/carbon black composites provide 4-5 times better fatigue strength due to the decrease of tan δ. SEM results also confirm fatigue results such that NR/carbon black composite has a relatively sharp and brittle fracture surface in comparison with NR/BR1/carbon black composite. Since BR gives more elasticity to NR/BR1 composite, the fracture process appears more ductile, and the crack propagation becomes more difficult than pure NR composite. Here, these results clearly show that blending carbon black reinforced NR or NR/SBR composites with BR which has different degrees of viscosity is quite favorable in terms of using these NR composites as anti-vibrational rubber bushings in automotive applications where high fatigue resistance and lower damping factor are important criteria.

Acknowledgments

Disclosure statement

No potential conflict of interest was reported by the authors.

References

[1] Legorju-jago K, Bathias C. Fatigue initiation and propagation in natural and synthetic rubbers. Int J Fatigue. 2002;24:85-92. https://doi.org/10.1016/S0142-1123(01)00062-7

[2] Creton C, Ciccotti M. Fracture and adhesion of soft materials: a review. Rep Prog Phys. 2016;79:046601. https://doi.org/10.1088/0034-4885/79/4/046601

[3] Mars WV, Fatemi A. Factors that affect the fatigue life of rubber: A literature survey. Rubber Chem Technol. 2004;77:391-412. https://doi.org/10.5254/1.354783

[4] Tee YL, Loo MS, Andriyana A. Recent advances on fatigue of rubber after the literature survey by Mars and Fatemi in 2002 and 2004. Int J Fatigue. 2018;110:115-129. https://doi.org/10.1016/j.ijfatigue.2018.01.00

[5] Findik F, Yilmaz R, Koksal T. Investigation of mechanical and physical properties of several industrial rubbers. Mater Design. 2004;25:269-276. https://doi.org/10.1016/j.matdes.2003.11.00

[6] Tangudom P, Thongsang S, Sombatsompop N. Cure and mechanical properties and abrasive wear behavior of natural rubber, styrene-butadiene rubber and their blends reinforced with silica hybrid fillers. Mater Design. 2014;53:856-864. https://doi.org/10.1016/j.matdes.2013.07.024

[7] Poompradub S, Tosaka M, Kohjiya S, Ikeda Y, Toki S, Sics I, et al. Mechanism of strain-induced crystallization in filled and unfilled natural rubber vulcanizates. J Appl Phys. 2005;97:103529. https://doi.org/10.1063/1.1900927

[8] Toki S, Fujimaki T, Okuyama M. Strain-induced crystallization of natural rubber as detected real-time by wide-angle X-ray diffraction technique. Polymer. 2000;41:5423-5429. https://doi.org/10.1016/S0032-3861(99)00724-7

[9] Huneau B. Strain-Induced Crystallization of Natural Rubber: A Review of X-Ray Diffraction Investigations. Rubber Chem Technol. 2011;84:425-452.

[10] Le Cam JB, Toussaint E. The Mechanism of Fatigue Crack Growth in Rubbers under Severe Loading: The Effect of Stress-Induced Crystallization. Macromolecules. 2010;43:4708-4714. https://doi.org/10.1021/ma100042n

[11] Mars WV, Fatemi A. Multiaxial stress effects on fatigue behavior of filled natural rubber. Int J Fatigue. 2006;28:521-529. https://doi.org/10.1016/j.ijfatigue.2005.07.040

[12] Mars WV, Fatemi A. Fatigue crack nucleation and growth in filled natural rubber. Fatigue Fract Eng M. 2003;26:779-789. https://doi.org/10.1046/j.1460-2695.2003.00678.x

[13] Le Cam JB, Huneau B, Verron E, Gornet L. Mechanism of fatigue crack growth in carbon black filled natural rubber. Macromolecules. 2004;37:5011-5017. https://doi.org/10.1021/ma0495386

[14] Saintier N, Cailletaud G, Piques R. Crack initiation and propagation under multiaxial fatigue in a natural rubber. Int J Fatigue. 2006;28:61-72. https://doi.org/10.1016/j.ijfatigue.2005.03.006

[15] Beurrot S, Huneau B, Verron E. In Situ SEM Study of Fatigue Crack Growth Mechanism in Carbon Black-Filled Natural Rubber. J Appl Polym Sci. 2010;117:1260-1269.

[16] Seichter S, Archodoulaki VM, Koch T, Holzner A, Wondracek A. Investigation of different influences on the fatigue behaviour of industrial rubbers. Polym Test. 2017;59:99-106. https://doi.org/10.1016/j.polymertesting.2017.01.018

[17] Saintier N, Cailletaud G, Piques R. Multiaxial fatigue life prediction for a natural rubber. Int J Fatigue. 2006;28:530-539. https://doi.org/10.1016/j.ijfatigue.2005.05.011

[18] Marco Y, Huneau B, Masquelier I, Le Saux V, Charrier P. Prediction of fatigue properties of natural rubber based on the descriptions of the cracks population and of the dissipated energy. Polym Test. 2017;59:67-74. https://doi.org/10.1016/j.polymertesting.2017.01.015

[19] Mars WV, Fatemi A A literature survey on fatigue analysis approaches for rubber. Int J Fatigue. 2002;24:949-961. https://doi.org/10.1016/S0142-1123(02)00008-

[20] George SC, Ninan KN, Groeninickx G, Thomas S. Styrene-butadiene rubber/natural rubber blends: Morphology, transport behavior, and dynamic mechanical and mechanical properties. J Appl Polym Sci. 2000;78:1280-1303. https://doi.org/10.1002/1097-4628(20001107)78:6<1280::AID-APP150>3.0.CO;2-S

[21] Varkey JT, Augustine S, Groeninckx G, Bhagawan SS, Rao SS, Thomas S. Morphology and mechanical and viscoelastic properties of natural rubber and styrene butadiene rubber latex blends. J Polym Sci Pol Phys. 2000;38:2189-2211. https://doi.org/10.1002/1099-0488(20000815)38:16<2189::AID-POLB120>3.0.CO;2-E

[22] Dong B, Zhang LQ, Wu YP. Influences of different dimensional carbon-based nanofillers on fracture and fatigue resistance of natural rubber composites. Polym Test. 2017;63:281-288. https://doi.org/10.1016/j.polymertesting.2017.08.035

[23] Wisojodharmo LA, Fidyaningsih R, Fitriani DA, Arti DK, Indriasari SH. The influence of natural rubber-butadiene rubber and carbon black type on the mechanical properties of tread compound. IOP Conf Series Mater Sci Eng. 2017;223:012013. https://doi.org/10.1088/1757-899X/223/1/012013

[24] Sreelekshmi RV, Sudha JD, Menon ARR. Novel organomodified kaolin/silica hybrid fillers in natural rubber and its blend with polybutadiene rubber. Polym Bull. 2017;74:783-801. https://doi.org/10.1007/s00289-016-1745-9

[25] Gao J, He Y, Gong X, Xu J. The role of carbon nanotubes in promoting the properties of carbon black-filled natural rubber/butadiene rubber composites. Results in Physics. 2017;7:4352-4358. https://doi.org/10.1016/j.rinp.2017.09.044

[26] Poikelispää M, Das A, Dierkes W, Vuorinen J. The effect of partial replacement of carbon black by carbon nanotubes on the properties of natural rubber/butadiene rubber compound. J Appl Polym Sci. 2013;130:3153-3160. https://doi.org/10.1002/app.39543

[27] Poikelispää M, Das A, Dierkes W, Vuorinen J. The effect of coupling agents on silicate-based nanofillers/carbon black dual filler systems on the properties of a natural rubber/butadiene rubber compound. J Elast Plast. 2015;47:738-752. https://doi.org/10.1177/0095244314538436

[28] Abdollahi M, Khanli HH., Aalaie, J, Yousefi M.R. Structure and properties of natural rubber/butadiene rubber (NR/BR) blend/sodium-montmorillonite nanocomposites prepared via a combined latex/melt intercalation method. Polymer Science Series A. 2011;53:1175-1181. https://doi.org/10.1134/S0965545X11120091

[29] Kim IJ, Kim WS, Lee DH, Kim W, Bae JW. Effect of nano zinc oxide on the cure characteristics and mechanical properties of the silica-filled natural rubber/butadiene rubber compounds. J Appl Polym Sci. 2010;117:1535-1543. https://doi.org/10.1002/app.31996

[30] Raji VV, Ramakrishnan S, Sukumar R, Brahmakumar M, Menon AR. Kaolin modified with sodium salt of rubber seed oil as a reinforcing filler for blends of natural rubber, polybutadiene rubber and acrylonitrile–butadiene rubber. Polymer International. 2015;64:1585-1593. https://doi.org/10.1002/pi.4956

[31] Liu XB, Gao Y, Bian L, Wang Z Influence of ultrafine full-vulcanized styrene-butadiene powdered rubber on dynamic mechanical properties of natural rubber/butadiene rubber and styrene-butadiene rubber/butadiene rubber blends. Polym Bull. 2015;72:2001-2017. https://doi.org/10.1007/s00289-015-1385-5

[32] Burgaz E, Gencoglu O, Goksuzoglu M. Rheological, mechanical and thermomechanical properties of carbon black reinforced natural rubber/butadiene rubber and natural rubber/butadiene rubber/styrene-butadiene rubber composites. Submitted to Research on Engineering Structures and Materials (RESM).

[33] Joseph AM, George B, Madhusoodanan KN, Alex R. Effect of Devulcanization on Crosslink Density and Crosslink Distribution of Carbon Black Filled Natural Rubber Vulcanizates. Rubber Chem Technol. 2016;89:653-670. https://doi.org/10.5254/rct.16.84819

[34] South JT, Case SW, Reifsnider KL. Effects of thermal aging on the mechanical properties of natural rubber. Rubber Chem Technol. 2003;76:785-802. https://doi.org/10.5254/1.3547772

[35] Nasir M, Teh GK The Effects of Various Types of Crosslinks on the Physical-Properties of Natural-Rubber. Eur Polym J. 1988;24:733-736. https://doi.org/10.1016/0014-3057(88)90007-9