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Research Article

# Carbon black reinforced natural rubber/butadiene rubber and natural rubber/butadiene rubber/styrene-butadiene rubber composites: Part I: Rheological, mechanical and thermomechanical properties

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Article Info	Abstract
Article history: Received 23 Nov 2018 Revised 12 Mar 2019 Accepted 18 Mar 2019	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 (higher viscosity and molecular weight) and branched chain structures. In NR/BR composite with a higher viscosity BR, the presence of both polysulphidic and monosulphidic types
Keywords: Natural rubber; Butadiene rubber; Styrene-butadiene rubber; Carbon black reinforced rubber composite; Thermomechanical properties; Rheological properties	of crosslinking was confirmed based on FT-IR data. NR/BR composite consisting of BR with higher viscosity has the lowest Payne effect and compression set values. NR/BR/SBR composites have much lower Payne effect values compared to NR/SBR system. Also, the addition of BR to NR decreases the tan $\delta$ value and leads to lowest values of tan $\delta$ in NR/BR composites. Tensile strength and elongation at break values in NR/BR/SBR composites are improved with the addition of BR with a lower viscosity. In comparison with NR/SBR, NR/BR/SBR composites exhibit much less compression set and stress relaxation values because NR/SBR composite exhibits more permanent deformation due to its more rigid styrene content. Here, these results clearly show that blending carbon black reinforced NR or NR/SBR composites with BR having different degrees of viscosity is quite favorable in terms of using these NR composites as anti- vibrational rubber bushings in automotive applications.

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#### 1. Introduction

The rheological, mechanical and thermomechanical properties of carbon black filled rubber composites are very important in terms of 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, highly improved mechanical and thermomechanical properties of rubber products can provide better driving dynamics, safety and reliability. Many reasons can affect the rheological, mechanical and thermomechanical properties of carbon black filled 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,

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automotive antivibration, sealants, adhesives & coatings, molded parts, body parts, spare parts, etc [5,6]. The strain-induced crystallization in NR increases mechanical properties especially under high amplitudes of strain. So, this behavior makes the natural rubber a unique elastomer in rubber industry [7-11].

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 [5,6,12,13]. SBR is generally used in wear applications. SBR is usually blended with NR to improve its tensile and tear properties [5,6,13]. 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, and rheological properties of NR/SBR composites have been studied by several researchers [5,6,12,13]. It was previously shown that tensile strength, elastic modulus, elongation at break, hardness and wear resistance of NR/SBR composites increase with increasing NR content and prevulcanization time [5,13].

It is well-known that unfilled or unreinforced rubber has a low modulus, poor abrasion resistance and fatigue behavior [3,4,14]. Carbon blacks (CBs) are generally used to improve the mechanical behavior of rubber. However, this reinforcing method is not adequate by itself especially in the fabrication of heavy industrial rubber products. Rubber composites that have close elastic modulus exhibit similar mechanical properties. BR increases chain flexibility at lower temperatures, filler loading capacity, and decreases heat-build up and energy consumption during mastication [1,3,4]. Thus, blending different types of natural rubber composite with BR is a typical method to improve mechanical properties [3,4,15,16]. 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 [15]. Furthermore, better mechanical properties in NR/BR composites were obtained by using carbon blacks that can be well dispersed in the rubber matrix [15]. Recently, the effects of using pyrolytic carbon black (CBp) and pyrolytic oil (Op) which were obtained from used tires on the rheological, mechanical and dynamic mechanical properties of NR/SBR blends were investigated and compared with a control sample that was prepared with N550 and commercial process oil [17]. It was shown that the curing and processing properties in CBp filled NR/SBR blends are similar with those of N550 filled system. In addition, the tensile strength, tear strength and modulus at 100% elongation of the NR/SBR vulcanizates decreased significantly with increasing amount of CBp [17]. Previously, the nanocrystalline cellulose (NCC) was used as a green alternative for carbon black in NR/BR/SBR blends, and the morphology, dynamic viscoelastic behavior, apparent crosslink density, mechanical and dynamic mechanical properties of NR/BR/SBR/NCC blends were discussed in detail [18]. Based on the results, it was shown that NCC was uniformly dispersed in composites and it exhibited comparable reinforcing effect with carbon black. In addition, mechanical tests revealed that the replacement of CB by NCC in NR/BR/SBR blends did not worsen mechanical properties of composites [18].

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/carbon black and NR/BR/carbon black composites. Among nano-sized filler containing NR/BR/carbon black composite studies in the literature, the use of carbon nanotubes (CNTs) [19,20], halloysite nanotube [21], nanoclay [21,22] and nano zinc oxide [23] in NR/BR/carbon black composite matrix can be given as examples. In addition, micron-sized silica [16,23], and organomodified kaolin [16,24] were used in NR/BR/carbon black composites to enhance the curing characteristics, fatigue resistance, mechanical and dynamic mechanical properties. The 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 [25]. Previously, the effect of a partial replacement of CB by silane-treated nanoclays and halloysite nanotubes on the properties of NR/BR blends was investigated [21]. Based on the results, it was concluded that the replacement of a small quantity of CB with silicates or nanotubes results in improved dispersion of the fillers and better dynamic properties due to the decrease of viscosity. However, the mechanical properties of NR/BR blends consisting of either silane treated silicates or halloysite nanotubes exhibited no improvement [21].

Previously, carbon black and carbon nanotube filled NR composites were prepared through an ultrasonic assisted latex mixing process, and their mechanical, rheological and dynamic mechanical properties were compared with NR composites that were prepared with the conventional mixing methods [26]. It was shown that the ultrasonic assisted latex mixing process leads to more homogenously distribution of CNTs in the matrix compared to the conventional mixing methods. Thus, the well dispersed CNTs and CB exhibited a synergistic reinforcing effect such that the elastic modulus at room temperature, storage modulus and complex viscosity increased whereas the maximum loss tangent and shear thinning index decreased with increasing CNT contents [26]. The influence of two types of CB filler N330 and N990 with primary particle sizes of 46 nm and 230 nm, respectively on acrylonitrile-butadiene rubber (NBR) elastomeric composites have been investigated [27]. Based on mechanical, rheological and thermal stability results, it was shown that N330 type carbon black reduces activation energy and increases overall curing rate, crosslinking density more than N990 type CB. N330 CB containing NBR elastomer composites exhibited more thermal stability than those consisting of N990 type CB due to the organic functional groups of carbon black surface which form strong interfacial adhesion forces between CB and the rubber matrix [27]. Previously, NR/BR blends in which the carbon black was replaced partially by multi-walled carbon nanotubes (MWCNTs) was prepared by blending of internal mixer and the two-roll mill [17]. Due to the synergistic effect of CNTs and CB, NR/BR elastomer composites consisting of both MWCNTs and CB exhibited higher values of abrasion resistance, modulus, crosslinking density, tear strength and thermal conductivity compared to those elastomers without any CNTs [17]. Recently, the effects of using 15 pphr sludge palm oil (SPO) as processing oil and various amounts of carbon black from 20 to 50 pphr as the reinforcing filler on the curing characteristics and mechanical properties of NR/SBR elastomeric composites were investigated [28]. The results showed that scorch and cure times, the tensile strength, modulus at 300% strain and tear strength of NR/SBR composites increase with the increasing carbon black loading [28]. Previously, halloysite nanotubes which were surface-modified by plasma polymerization were used as fillers in CB filled NR/BR composites [29]. Based on the results, it was shown that a thiophene modification of HNTs led to improved mechanical properties due to the formation of special type of clusters with carbon black particles and resulted in lower values of Payne effect indicating better filler-polymer interactions [29].

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 (higher molecular weight and viscosity) and branched chain structures. 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 the curing behavior, mechanical and thermomechanical properties of NR/BR, NR/SBR and NR/BR/SBR blends. 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 and viscosities display significant 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 curing behavior, mechanical and thermomechanical 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, -58 and -92°C, respectively. The composition of NR composites is given in Table 1.

Sample	NR	SBR	BR1	BR2
Composition	(phr)	(phr)	(phr)	(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 1 The composition of NR composites (BR1: Buna CB22, BR2: Buna CB24)

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		

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.

## 2.2 Fabrication of carbon black filled rubber composites

All samples were mixed in an open laboratory mill that has two rolls. 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. Dispersion qualities of NR samples were analyzed with Alpha disperGRADER<sup>™</sup> according to ASTM 7723 standard.

Table 3	The dispersion levels and dynamic viscosities of uncured master batches of NR
composi	tes

Sample Composition	NR	NR/ SBR	NR/ BR1	NR/BR1/ SBR	NR/ BR2	NR/BR2/ SBR
Mean Agglomerate Size (µm)	10.4	7.8	7.9	8.5	8.8	9.4
n* @ 0.1 Hz (Pa.s)	79980	83752	120385	94211	105812	122660

The dispersion results are given in Table 3. These results show that dispersion levels in all the samples are very close to each other. Master batches were rested for 24 hours after the mastication process. Then, the viscosity of master batches was characterized *via* rheometer at 0.1 Hz under constant strain to verify whether NR composites were overmasticated or not. The rheometer results showed that dynamic viscosities of NR composites are in the range of acceptable tolerances. Afterward, vulcanization agents were added to NR composites. Samples of NR composites were molded by using the compression molding at 180°C within the appropriate cure time. The optimal curing for each NR composite was achieved according to t90 values that were obtained from rheometer results.

#### 2.3 Physical/Chemical Characterization

#### 2.3.1. Attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectroscopy

The Attenuated total reflectance Fourier transform infrared (ATR FT-IR) analysis was performed using a Perkin Elmer branded Spectrum two FT-IR spectrometer, with a germanium crystal having a 9300:1 SNR. The sample surface was scanned in the 4000–600cm<sup>-1</sup> range, at 45° angle. The ATR-FT-IR spectra were recorded at room temperature. The background subtraction and baseline correction were done.

#### 2.3.2. Rheological analysis

Rheometer tests were performed by using Alpha rubber process analyzer 2000 (RPA) to characterize the curing dynamics of NR composites. Curing parameters such as ts2, t90, G', G", mL, mH, Payne effect were analyzed as a function of time by RPA at 180°C. The Payne effect values of NR composites were calculated by subtracting G' at angle 25% from G' at angle 1%. Results are given in Table 4. For each RPA test, the sample weight is 8 g.

#### 2.3.3. Hardness

Shore A hardness of rubber samples was measured by using a Bareiss Digitest II type hardness testing machine. The diameter and thickness of the samples are 40 and 6 mm, respectively. Hardness values were recorded after 5 seconds of loading.

#### 2.3.4. Tensile testing

For tensile tests, dumbbell shaped samples of NR composites with 33 mm gauge length were molded by compression molding at 180°C. Tensile tests were performed by using a Zwick 2.5 kN Z2.5/TN1P universal testing machine in accordance with the DIN 53504 standard. The cross head tensile speed was 200 mm/min at room temperature. Five samples were tested for each NR composite, and they were averaged to determine the tensile strength.

#### 2.3.5. Stress relaxation and compression testing

The compression set and stress relaxation in compression tests were analyzed by using Elastocon EB 20 HT and Elastocon EB 17 HT instruments, respectively. The cylindrical sample dimensions for the compression set experiments have a diameter of 12 mm and a thickness of 6.30 mm. The ASTM Standards D395-16 and D6147-97 were used for the compression set and stress relaxation experiments, respectively. All tests were performed at 70°C for 72 hours in Elastocon ovens.

#### 3. Results and Discussion

FT-IR results of NR composites are given in Fig.1(a). The vibration that belongs to the isoprene functional group is located at 840 cm<sup>-1</sup> [30]. The vibration peaks that are located between 3000-2800 cm<sup>-1</sup> correspond to asymmetric and symmetric stretchings of C=CH, CH<sub>2</sub>, CH<sub>3</sub> groups in NR [30]. The vibration peaks at 1447 and 1377 cm<sup>-1</sup> correspond to asymmetric deformation vibrations of CH<sub>2</sub> and CH<sub>3</sub> groups in NR [30]. The characteristic in-plane bending of C=C-H is generally observed at 1288 cm<sup>-1</sup> [30]. However, in Fig.1(a), this peak appears at 1265 cm<sup>-1</sup> due to different degrees of interactions between isoprene chains and added small chemicals.



Fig. 1(a) ATR FT-IR of NR, NR/BR, NR/SBR and NR/BR/SBR composites in the region of 4000-600  $\rm cm^{-1}$ 

In analogous with NR composite, vibration bands at 3000-2800 cm<sup>-1</sup> correspond to asymmetric and symmetric stretchings of C=CH, CH<sub>2</sub>, CH<sub>3</sub> groups in NR/SBR composite. The vibrations at 1493 and 1451 cm<sup>-1</sup> correspond to stretchings of carbon atoms in the

aromatic ring. Stretching vibrations at 1074 and 1029 cm<sup>-1</sup> correspond to styrene and *cis*-Polybutadiene units, respectively [31]. The vibration peaks that are located at 759 and 699 cm<sup>-1</sup> correspond to deformation and out-of-plane bending of CH groups in the aromatic ring, respectively [30]. In NR/BR composites, the characteristics peak at 3024 cm<sup>-1</sup> corresponds to stretching vibration of the CH<sub>2</sub> groups in butadiene units. The peaks that are located at 1666 and 1400 cm<sup>-1</sup> are strong proofs for the existence of C=C bonds and deformation vibration of (=CH) units that exist in butadiene units, respectively [30,31].



Fig. 1(b) ATR FT-IR of NR, NR/BR, NR/SBR and NR/BR/SBR composites in the region of 2000-600 cm<sup>-1</sup>

As observed in Fig. 1(b), typical peaks in the range 700-600 cm<sup>-1</sup> are due to C–S–C, C–S and S–S bonds, respectively. The C–S vibration appears at a frequency higher than S–S vibration since C–S bond stability is higher than S–S [32,33]. Monosulphide linkages occur at higher frequencies that are close to 700 whereas polysulphide vibration bands usually appear around 661 and 600 cm<sup>-1</sup> [32,33]. In NR-BR1, two vibration bands that are located at 667 and 691 cm<sup>-1</sup> are associated with polysulphide and monosulphide bonds, respectively. The vibration band at 667 cm<sup>-1</sup> is much stronger compared to the peak at 691 cm<sup>-1</sup>. This result confirms that polysulphide type of crosslinking is dominant in NR/BR1. In NR/SBR, in the range 700-600 cm<sup>-1</sup>, two vibration peaks that are located at 698 and 666 cm<sup>-1</sup> are clearly visible. Here, the vibration band at 698 cm<sup>-1</sup> is much stronger compared to the peak at 666 cm<sup>-1</sup>. This result confirms that monosulphide type of crosslinking is dominant in NR/SBR.



Fig. 2 Cure characteristics of carbon black filled NR, NR/BR, NR/SBR and NR/BR/SBR composites

The rheometer results of NR composites at 180°C are shown in Fig. 2. The cure rates of NR composites were calculated and given in Table 4. In addition, rheometer results of similar NR vulcanizates from literature are also given in Table 5 for comparison.

Sample	NR	NR/	NR/	NR/BR1/	NR/	NR/BR2/
Composition		SBR	BR1	SBR	BR2	SBR
ts2 (min)	0.80	1.17	1.42	0.90	1.33	1.04
t90 (min)	1.63	2.32	3.05	2.06	2.76	2.81
mL (dNm)	0.15	0.80	1.43	0.84	1.49	1.17
mH (dNm)	11.67	12.47	12.32	10.75	14.58	11.78
mH-mL	11.52	11.67	10.89	9.91	13.09	10.61
(dNm)						
Cure Rate	13.88	10.15	6.68	8.54	9.15	5.99
(dNm/min)						
G' (kPa)	1575	1590	1247	1310	1428	1266
(angle 1%)						
G' (kPa)	695	892	900	791	980	900
(angle 25%)						
G' (kPa)	439	555	596	514	680	617
(angle 100%)						
Payne Effect	880	698	347	519	448	366
(kPa)						
Tan δ	0.139	0.124	0.082	0.129	0.077	0.155

Table 4Rheometer results of NR vulcanizates

Sample	NR(100phr)	NR(50phr)/	NR(85phr)/	NR(70phr)/
Composition	(ref15)	SBR(50phr)	BR(15phr)	SBR(30phr)
		(ref12)	(ref15)	(ref12)
ts2 (min)	3.23	5.54	3.58	5.05
t90 (min)	9.47	11.40	8.65	10.23
mL (dNm)	2.65	0.65	2.70	0.53
mH (dNm)	15.66	6.72	15.25	6.09
mH-mL	13.01	6.07	12.55	5.56
(dNm)				
Cure Rate	16.02	17.06	19.72	19.30
Index (min <sup>-1</sup> )				

Table 5 Rheometer results of similar NR vulcanizates from literature

Based on rheometer results, the smallest and highest cure rate values were obtained for samples NR/BR2/SBR and NR, respectively. The most optimized cure rate was achieved in NR/BR1/SBR composite. In application, the crosslink density of rubber vulcanizates can be evaluated by help of difference between mH-mL terms. All NR composites have optimal crosslink densities that can be observed from their mH-mL values. The crosslink density increases the fatigue life of rubber composites since it depends on how many polymer chains are linked to each other. Once crosslinking reaction occurs, these chemical links cannot be broken easily. Also, the vulcanization system directly affects the fatigue resistance and compression set since it determines sulfur bridges with mono or poly structures. Monosulphidic bridges (-S-) induce strong and short crosslinking distances but they have no ability to make bonding again when they are broken in contrast to polysulphidic bridges (-S-S-S-) [34]. All rubber composites almost have the same modulus since their G' (angle %25) values are close to each other. In Table 4, NR/BR1 has the lowest Payne effect value since the mean agglomerate size of carbon black in NR/BR1 was measured as one of the lowest in Table 3. This result shows that the addition of BR to NR improves the quality of filler dispersion due to favorable interactions between carbon black and polymer chains. Also, in Table 4, based on the tan  $\delta$ , the addition of BR to NR decreases the tan  $\delta$  value. Especially, NR/BR1 and NR/BR2 rubber composite samples have the lowest values of tan  $\delta$ . So, the addition of BR to carbon black filled NR composite decreases the viscous property and increases the elastic property.

In comparison with NR/SBR composite, NR/BR1/SBR and NR/BR2/SBR composites exhibit much lower S curves in terms of their mH values. In addition, rheometer curves of NR/BR1/SBR and NR/BR2/SBR composites are very similar to each other. In this respect, 20 phr butadiene addition to NR/SBR composite does not improve the curing behavior in these composites. Furthermore, compared to NR/SBR composite, NR/BR1/SBR and NR/BR2/SBR soften or their max torque (mH) values decrease since the total SBR amount decreases with the addition of 20 phr of BR.



Fig. 3 Tensile testing results of NR, NR/BR, NR/SBR and NR/BR/SBR composites.

The results of tensile tests are given in Fig.3. Here, the tensile strength does not really change, but the elongation at break of pure NR increases with the addition of BR2 which has a highly branched chain structure. This result can be explained such that polymer-filler interactions increase with the well-mixing of carbon black due to the lower viscosity and molecular weight of BR2. Thus, the increase in polymer-filler interactions leads to increase both in terms of tensile strength and elongation at break. In comparison with NR/SBR composite, the tensile strength of NR/BR1/SBR decreases since the phr value of SBR decreases more in this composite. Furthermore, the tensile strength of NR/BR1/SBR is lower than that of NR/SBR because SBR is more rigid than BR1 due to its 23% styrene content. Also, the tensile strength of NR/BR2/SBR composite is lower than that of NR/SBR.

Sample	NR(100phr)	NR(50phr)/	NR(80phr)/	NR(60phr)/
Composition	(ref35)	SBR(50phr)	BR(20phr)	SBR(40phr)
		(ref17)	(ref29)	(ref28)
Tensile strength	30	27	20.6	18
(MPa)				
Elongation at	490	325	443	750
break(%)				
Modulus at 100	3.1	1.68	2.5	-
%(MPa)				
Modulus at 300	-	4.62	12.1	5
%(MPa)				
Compression set	-	31	-	-
(%)				

Table 6 Tensile and compression testing results of similar NR vulcanizates from literature



Fig. 4 Compression set and hardness results of NR, NR/BR, NR/SBR and NR/BR/SBR composites.

The results for compression set behavior and hardness measurements are given in Fig. 4. The compression set behavior is also used to determine how elastic a rubber composite behaves under static load. If the chemical bonds are strong enough, compression set results show less permanent deformation. As can be seen from Fig.4, NR/BR1 composite has the lowest compression set behavior. Therefore, based on the compression set data, NR/BR1 composite can be evaluated as the most elastic blend. Hardness values of all NR composites are very similar to each other. Hardness values of all NR composites are very similar to each other. This result mainly shows that changing the composition of NR, BR and SBR in the rubber composites does not affect the hardness values that much. The hardness values of rubber composites is mainly dictated by the amount of carbon black that is used in these samples. In all the samples, carbon black amount is fixed as 50 phr. So, for this reason, it is very logical that the hardness values of rubber composites does not exhibit any big change. The compression set is directly related to Payne effect, viscosity of the polymer and vulcanization system. In comparison with NR/SBR, NR/BR1/SBR and NR/BR2/SBR composites exhibit much less compression set values because NR/SBR composite exhibits more permanent deformation due to its relatively higher rigid styrene content.

Stress relaxation behavior is given in Fig. 5. Stress relaxation is directly related with the elastic characteristics of sulphur bonds which are located between polymer chains [34,36,37]. Single bridges of sulphur (monosulphidic bridges) are known as more elastic and reliable in terms of chemical bonding [34,37]. 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) [34,37]. In addition, broken monosulphidic bonds have less possibility in terms of bonding again spontaneously in contrast to polysulphidic bonds [34,37]. 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 and superior thermomechanical properties at the same time.



Fig. 5 Stress relaxation results of NR, NR/BR, NR/SBR and NR/BR/SBR composites.

NR/SBR composite displays a much more higher stress relaxation value in comparison with other rubber composites since it experiences a much higher force loss due to its higher rigidity. In comparison with NR/SBR, NR/BR1/SBR and NR/BR2/SBR composites exhibit much lower stress relaxation values. Unlike expectations, in Fig. 5, stress relaxation values of NR/BR1/SBR and NR/BR2/SBR composites are almost equal to each other. It is expected that the ternary blend consisting of BR1 should experience a much more force loss due to its higher viscosity. However, this difference in terms of viscosity does not reflect on the stress relaxation behavior since the vulcanization system has a much more dominant effect on the compression set and stress relaxation at higher temperatures.

# 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 (higher viscosity and molecular weight) and branched chain structures. Rheological, mechanical and thermomechanical properties of carbon black filled NR/BR, NR/SBR and NR/BR/SBR composites were systematically compared with each other. Based on rheometer results, the most optimized cure rate was achieved in NR/BR1/SBR composite. NR/BR1 composite has the lowest Payne effect value since the mean agglomerate size of carbon black in NR/BR1 was measured as one of the lowest based on dispersion results. Thus, the addition of BR to NR improves the quality of filler dispersion due to favorable interactions between carbon black and polymer chains. Also, the addition of BR to NR decreases the tan  $\delta$  value and leads to lowest values of tan  $\delta$  in NR/BR composites. In comparison with NR/SBR composite, the tensile strength of NR/BR1/SBR decreases since the phr value of SBR decreases more in this composite. Furthermore, the tensile strength of NR/BR1/SBR composite is lower than that of NR/SBR because SBR is more rigid than BR due to its 23% styrene content. Based on the compression set data, NR/BR1 composite has the lowest compression set behavior with an optimal crosslink type and density. In comparison with NR/SBR, NR/BR1/SBR and NR/BR2/SBR composites exhibit much less compression set values because NR/SBR composite exhibits more permanent deformation due to its more rigid styrene content. In comparison with NR/SBR composite, NR/BR1/SBR and NR/BR2/SBR exhibit much lower stress relaxation values. In agreement with compression set values from compression testing data and tan  $\delta$  values from rheometer data, the elastic character increases and the viscous property decreases in carbon black filled NR/BR composites with the addition of BR. Here, these results clearly show that blending carbon black reinforced NR or NR/SBR composites with BR having different degrees of viscosity is quite favorable in terms of using these NR composites as anti-vibrational rubber bushings in automotive applications.

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