MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

Preparation and Application of Chemically Bonded Silica Supported Calix[4]arene as Reinforced Filler in NR/BR Blend Based Rubber Compounds

Hediye Mohamadi[a], Fereshte Motiee[a],*, Mandana Saber Tehrani[a], and Saeed Taghvaei-Ganjali[a]

[a] Chemistry Department, IA-University, North Tehran Branch, Tehran 1651153311, Iran
*e-mail: f_motiee@iau-tnb.ac.ir

Abstract—In this study, we tried to reduce polarization of silica surface by chemically bonding cholorosulfonyl calix[4]arene (CSC[4]A) and silica (Si–O–Cl) to improve dispersion between filler and elastomer. To confirm synthesis of CSC[4]A, ^{1}H NMR, ^{13}C NMR, and IR spectrophotometry were used. Obtained composite of chemically bonded silica and CSC[4]A was characterized by TGA. Compounds (contained silica, silica and silane, silica-calix system) were prepared to investigate the effect of silica-calix system (CSC[4]A–SiO$_2$) on the rheological and mechanical properties of rubber compounds based on natural rubber/*cis*-butadiene rubber (NR/BR) blend in tire tread formulation. The rheological and mechanical properties of three samples were investigated by different devices and a surface morphology was evaluated by FESEM technique. The results revealed that the curing behavior of the compound with CSC[4]A–SiO$_2$ did not significantly differ from other compounds, while reversion was considerably reduced compared with that to other compounds. Also, the mechanical properties of compound with CSC[4]A–SiO$_2$ were improved dramatically especially in fatigue resistance.

Keywords: Supramolecular structure, mechanical properties, rheology, morphology, rubber blend

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INTRODUCTION

Silica is widely used in rubber industries as reinforcement filler especially in green tire and colored rubber compounds [1]. The use of silica improves tensile strength, tear strength, and wet grip and also reduces rolling resistance of produced tire [2, 3]. The functional groups on the silica surface play an important role in the final properties of rubber products. However silica has the disadvantages: (1) silanol groups on the silica surface are hydrophilic and therefore it is incompatible with the hydrophobic rubber bases; (2) Formation of hydrogen bonding in silica–silica system which results in the aggregation of silica particles; (3) Adsorption of cure ingredients, such as zinc oxide, which reduces the curing efficiency and decreases the crosslinking density; (4) The acidic surface of silica causing adsorption of accelerators and consequently increasing scorch time [4].

To solve these problems, in recent years, it has been attempted to improve the interaction between silica and elastomer by modification of silica surface or changing the elastomer surface. In 2015, cardanol was bound to the natural rubber to alter its surface. Cardanol contains phenolic groups so the interaction between siloxane groups of silica and the polar section of cardanol leads to improving silica reinforcement properties, an increase in wear resistance and a decrease in compression set [5]. In 2017, the SBR elastomer surface was optimized by using glycidyl methacrylate (GMA) and emulsion polymerization, so epoxy functional groups were bonded to the SBR elastomer surface. The interaction of the epoxy functional groups of elastomer and hydroxyl groups of silica improves the silica distribution, reduces the rolling resistance, increases wet grip, and also improves the mechanical properties of the compound [6].

In the rubber industry, one of the most important solution to change the silica surface is using of coupling agent. Coupling agents are bi-functional compounds that one side reacts with the elastomer and the other side reacts with silica so it relults in forming a bridge between silica and polymer matrix. Coupling agents improve processability, tensile strength, and abrasion resistance, but they are expensive [7]. Zhong et al. used (3-glycidoxypropyl)trimethoxysilane as a modifier in order to optimize the silica surface. Using this system as a filler in SBR elastomer contributed to improves filler dispersion. The interaction between the elastomer and the filler increases the efficiency of accelerator and increments the mechanical properties of the compound [8].

Calixarenes are cavity-shaped cyclic molecules consisting of phenol units linked via alkylidene groups [9, 10]. Calixarenes are prepared by the base-catalyzed reaction of formaldehyde with phenol derivatives [11]. The lower rims of calixarenes are phenol units, which provide excellent sites for the introduction of other derivative moieties, and the *tert*-butyl groups of calixarenes can be easily removed, enabling a variety of reactions for the introduction of functional groups on the upper rim [12]. Although calixarenes have many applications in adsorption [13, 14], separation [15], sensors [16], ion selective membrane electrodes, construction of polyurethane foams and composite, and remove ions [17–21], little work has been carried out on the utility of calixarenes as filler in the rubber industry.

In 2017, Li et al. prepared C-methyl calix[4] resorcinarene-2 (CMCR-2) with four hexyl thiol methyl chains and used it as antioxidants in natural rubber composites. They compared thermal stability of calixarene with commercial antioxidants [2,6-di-*tert*-butyl-4-methylphenol (BHT)]. The results revealed that CMCR-2 acts as an outstanding antioxidant compare to conventional BHT [22]. In 2010, some researchers used calixarene as a coupling agent in tire compounds without any chemical bonding. They have used two coupling agents in NR/SBR blend and have compared them with commercial coupling agent Si69. The coupling agents were 5,11,17-tri-*tert*-butyl-23-trimethylsilylethynyl-25,26,27,28-tertapropoxycalix[4]arene and decyloxytriethylsilane. The results shown that comparing with calixarene [4], Si69 and decyloxytriethylsilane improve physicomechanical properties. In 2012, for the first time, Taghvaei et al.

synthesized silica supported calix[4]arene (CSC[4]A–SiO$_2$) [23]. They reported in 2018 that 0.2 g CSC[4]A–SiO$_2$ could remove 49 and 55% of CBS, DPG, which are widely used in rubber industries as additives in rubber compounds. Their investigations also showed that CSC[4]A–SiO$_2$ can act as shift reagent in NMR spectroscopy [14].

In this paper 25,26,27,28-tetrahydroxy-5,11,17,23-tetrakis[cholorosulfonyl]calix[4]arene (CSC[4]A) was chemically bonded to silica (CSC[4]A–SiO$_2$) for modification of silica surface and applied as a dispersed filler in the NR/BR blend based rubber compound. The effect of this filler is studied on dynamic and mechanical properties of rubber compounds in tire tread formulation. The results show that CSC[4]A–SiO$_2$ acts as fair dispersed filler and improves dynamic and mechanical properties of NR/BR blend based rubber compound in tire tread.

EXPERIMENTAL

Chemicals and reagents. ULTRASIL*VN3 GR as a precipitated silica (with particle size 180 m^2 g^{-1}) was purchased from the industrial source. Para-*tert*-butyl phenol, diphenylether, sodium hydroxide, dichloromethane, chlorosulfonic acid, diethyl ether, hydrochloric acid were purchased from Merck (Germany) company, and ethyl acetate, acetic acid, acetone, xylene, formaldehyde were purchased from Mojalali (Iran) company. All solvents were dried before using.

Equipment. Electrothermal 9200 device was used to determine melting points. ATR-FTIR spectra were obtained using a BRUKER TENSOR 27 (German Co). SINCO STA 1500 (TGA/DSC) was used for the TGA of the prepared samples. The NMR spectrum were obtained from Bruker AM-500 MHz with TMS as internal standard for ^{1}H NMR and Bruker AM-125 MHz with TMS as internal standard for ^{13}C NMR spectroscopy.

Synthesis of 5,11,17,23 tetra-*tert*-butylcalix[4] arene. To a 3-necked round bottom flask equipped with a thermometer and mechanical stirrer 100 g (about 0.66 mol) of powder *p-tert*-butyl phenol and a solution of 33.3 g of sodium hydroxide in 100 mL formaldehyde (37%) were added and the solution was heated at 120°C for 2 h. At the end of this period, the reaction mixture converts to a viscose and yellow mass. The reaction mixture was cooled to room temperature and 800 mL

of diphenylether was added and stirred for 1 h at room temperature. For exiting steam of water, the nitrogen inlet was set to the flask and one of the necks was kept open, the flask was put in oil bath and was heated for 1 h at 120°C. When water was removed, the inlet nitrogen was left off of the setup and condenser was set. The mixture was refluxed at 250°C for 2 h. In this period gray color converts to brown and black. The reaction mixture was cooled to room temperature and ethyl acetate was added to the flask and stirred for 30 min at room temperature. When the mixture stirred the suspended powder was observed. The mixture was left for 2 days and then was filtered. The precipitate was washed by ethyl acetate, acetic acid, distilled water, and acetone. The crystal and white precipitate was obtained.

Yield: 64%; mp 342–344°C; ATR-FTR: υ_{max} (cm^{-1}) = 3169, 2955,1200,1401; ^{1}H NMR (400 MHz, CDCl$_3$, δ):1.21 (s, 36H, [CH(CH$_3$)$_3$], 3.52 (d, 4H, ArCH$_2$Ar, J 12.8 Hz), 4.27 (d, 4H ,ArCH$_2$Ar, J 12.8 Hz), 7.05 (s, 8H, Ar–H),10.34 (s, 4H, OH); ^{13}C NMR: (100 MHz, CDCl$_3$, δ): 31.5, 32.5, 34.0, 126.1, 128.6, 144.5, 146.8.

Synthesis of 25,26,27,28-tetrahydroxy-5,11,17,23-tetrakis[cholorosulfonyl]calix[4]arene (CSC[4]A). 8 g of calix[4]arene synthesized in previous section and 280 mL of dry dichloromethane were poured to a 3-necked round bottom flask and were stirred for 30 min. A condenser was installed in the flask and inlet nitrogen was fed to the flask; the flask was placed in the ice bath until reaching –5…–10°C. When chlorosulfonic acid (48 mL) was exhausted the mixture was refluxed for 1 h. Biethyl ether (700 mL) was added to the mixture at room temperature and stirred for 1 h. The precipitate was filtered and washed by diethyl ether.

Yield 50%; mp > 230°C; ATR-FTIR: υ_{max},(cm^{-1}) = 2881, 2829,1455, 1936, 650, 455-1000. ^{1}H NMR (500 MHz, DMSO-d_6, δ): 3.96 (s, 8H, ArCH$_2$Ar), 7.39 (s, 8H, Ar-H), 11.37 (s, 4H, OH); ^{13}C NMR (125 MHz, DMSO-d_6, δ): 30.6 (ArCH$_2$Ar), 126.5 (Ar–H), 127.3 (Ar–CH$_2$), 138.3 (Ar–SO$_2$), 151.6 (Ar–OH).

Silica activation. Industrial silica (10 g) was activated by refluxing with 200 mL hydrochloric acid for 4 h at room temperature to remove any adsorbed metal ions. The mixture was filtered and silica precipitate was washed by distillated water and dried at 150°C for 6 h.

Synthesis of cholorosulfonylcalix[4]arene bonded silica (CSC[4]A–SiO$_2$). A mixture of activated silica (10 g), chlorosulfonylcalix[4]arene(1 g), and xylene

(350 mL) was placed in a 3-necked round bottom flask equipped with a thermometer, a reflux condenser, and outlet tube for conducting of HCl gas to a flask that contains silver nitrate solution. The mixture was stirred and refluxed at 140°C for 72 h. Afterward, the mixture was filtered and washed with dichloromethane, diethyl ether, methanol, and acetone. The gray mass was obtained, which was refluxed with acetone for 12 h in a soxhlet system. Then the precipitate [CSC[4]A–SiO$_2$] was dried at 150°C for 12 h. Obtained compound of chemically bonded silica and CSC[4]A was characterized by TGA. The TGA curve of CSC[4]A–SiO$_2$ consists of two stages of weight loss. The first stage is between 30 and 110°C, which can be related to remaining solvents and water molecules enclosed in the silica network. The second stage is between 200 to 900°C, which can be attributed to the decomposition of chemically stabilized groups on the activated silica gel surface.

Preparation of rubber compounds based on NR/BR blend using in tire tread formulation. In this study, three compounds were used (their formulation are shown in Table 1). In compound A, silica without coupling agent was used as filler. In compound B, silica was as filler and silane was as the coupling agent. In compound C, the CSC[4]A–SiO$_2$ was used as dispersed filler without coupling agent. All compounds were mixed in open two roll mixing mill at 60–70°C and the rubber compounds were cured at 160°C.

MEASUREMENTS

Cure characteristics. The cure characteristics of three compounds were determined at 160°C using a Monsanto Moving Die Rheometer HIWA900 MDR (HIWA Engineering Co., Iran), which was utilized to determine the scorch time (ts$_2$), cure time (t$_{90}$) ,cure rate index (CRI), the torque difference (MH–ML), and reversion according to ASTM D5289. The results of rheometer were summarized in Table 2 and Fig. 1.

Physicomechanical properties. Tensile tests were determined on a Testometric M350 at room temperature. The modulus, elongation, and tensile strength of vulcanizes were determined according to ISO 37. Hardness was measured in terms of Shore A (Bareiss) according to ASTM D2240. Resilience was carried out by Hiwa300 (HIWA Engineering Co., Iran) according to DIN 53512 and fatigue resistance was studied by Hiwa600 (HIWA Engineering Co., Iran) according to

Table 1. Compound Formulations

Ingredient	Concentration, phr[a]		
	A	B	C
NR	70	70	70
BR	30	30	30
Carbon Black 660	46	46	46
Aromatic Oil	15	15	15
Silica Ultrasil VN3	17	17	–
CSC[4]A–SiO$_2$	–	–	17
Silane	–	0.5	–
ZnO	3	3	3
Stearic acid	1	1	1
TMQ	1	1	1
6PPD	1	1	1
TBBS	1.75	1.75	1.75
Sulfur	1.4	1.4	1.4
Wax	2	2	2

[a] phr represented the mass parts per 100 mass parts of NR/BR blend.

ISO 6943.

Scanning electron microscopy. The field emission scanning electron microscopy (FESEM) images of composites were obtained using a TESCAN MIRA3 scanning electron microscope to obtain information re-
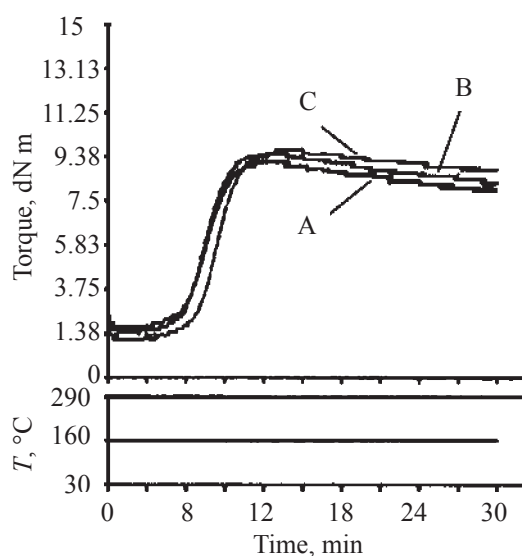

Fig. 1. Rheogram of rubber compounds (a) A, (b) B, (c) C. (T) Temperature, °C.

garding the filler dispersion (Fig. 2). The cross section images of samples were obtained by dipping and fracturing the prepared composites in liquid nitrogen and then covered with the layer of gold before analysis

RESULTS AND DISCUSSION

Morphological studies (structural analysis of vulcanizate). In order to study the morphology of each compound, FESEM images were taken (Fig. 2). Surveying the surface morphology of sample C compared to two other samples shows a uniform and homogeneous surface, which can be due to the appropriate mixing of various components of the blend, including the dispersion of new filler within the polymer matrix.

Curing characteristics. The results obtained from the curing behavior of compounds based on NR/BR blend and filled with silica (A), silica and silane (B), CSC[4]A-SiO$_2$ (C) demonstrated that the optimum curing time (t_{c90}) and scorch time (t_{s2}) of sample C were slightly increased. As a result, the cure rate index (CRI) has released. Data obtained from rheometry curve showed that reversion decreases in compound C, which can be a major achievement in this project. Studies have shown that the sulfur-accelerator vulcanization curve consists of three periods. The first period is scorch time. During the scorch time, zinc oxide reacts with stearic acid and generates zinc stearate.

$$ZnO + CH_3(CH_2)_{16}COOH$$
$$\rightarrow Zn[CH_3(CH_2)_{16}COO]_2 + H_2O.$$
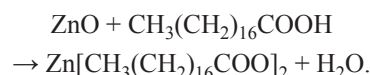
In the presence of zinc stearate and heat, elemental sulfurs convert to polysulfide radicals as shown in Fig. 3. On the other hand the presence of fatty acid carboxylate causes to provide tetra functional zinc- accelerator (Zn-acc) complex. In the next step polysulfide radicals react with Zn-acc complex and the obtained product reacts with active sites of rubber chains to form chemical crosslink.

No crosslinks form during scorch time and torque remains unchanged providing a safe processing time. In the second period, the formation of crosslinks begins and torque has increased until reaching the optimum cure time. In the third period, three positions may occur: (1) The formation of crosslink proceeds, which is most commonly found in Neoprene rubber, and is called as marching modulus; (2) The formation of crosslink remains constant and does not change over time. This state
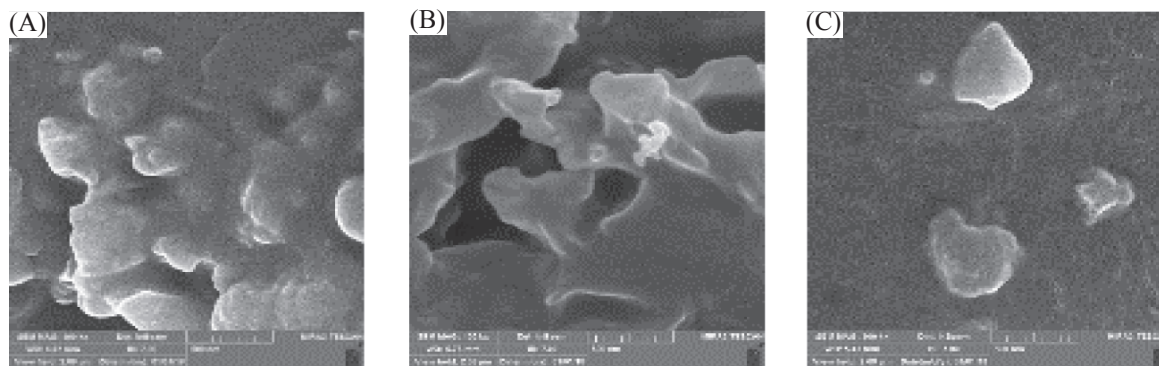
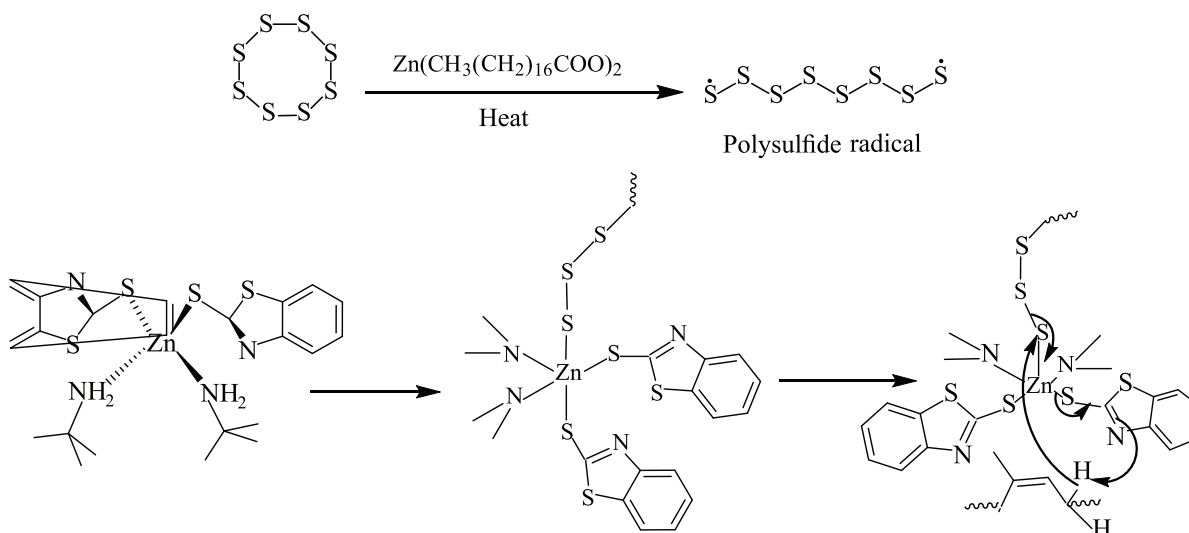**Fig. 2.** FESEM (500 nm) for rubber compounds A–C.

Fig. 3. Mechanism of sulfur crosslinks formation [1].

occurs more often in SBR rubber and is called as equilibrium modulu;. (3) Crosslinks, especially polysulfide links, whose thermal stability is less than other types of crosslinks, begin to fracture (reversion), it occurs often in NR rubber [23–25]. The vulcanization behavior of sample C (CSC[4]A–SiO$_2$) indicates an increase in scorch time (t_{s2}) and optimum cure time (t_{c90}), consequently, the cure rate index (CRI) decreases. Since the formation rate of Zn-acc complex determines the cure rate index, scorch time, optimum cure time, according to calixarene cavity, it is predicted that: (1) A novel accelerator is generated by physical interaction between conventional accelerator and calixarene. Therefore new accelerator based on special shape of calixarene (leading conventional accelerator to be trapped on cavity of calixarene) has not been able to form the Zn-acc complex as fast as before; (2) Vulcanization involves diffusion of

Zn-acc complex through an elastomer, so the large surface area of Zn-acc complex affects the rate of vulcanization and reduces the vulcanization time [24, 26]. The new Zn-acc complex has huge molecular weight so this causes to decrease cure rate index and increases scorch time and optimum cure time.

The second results were listed in Table 2, the delta torque value of compound C increases in comparison with compound B (about 5%) and compound A (about 12%). These results show that in the presence of CSC [4] A–SiO$_2$, the curing rate has dropped but the crosslink density has not decreased (it seems to have increased slightly). It shows that the novel accelerator plays its role with a bit of delay.

Curing behavior of three specimens shows the reversion behavior for all samples but reversion in

Table 2. Cure characteristics of rubber compounds A–C

Compound	t_{c90}, min	t_{s2}, min	CRI	MH, dN m	ML, dN m	MH–ML, dN m	Rev, dN m	(Rev/MH) × 100
A	9.36	6.83	37.39	9.10	2.07	7.04	0.28	3.1
B	9.32	6.69	35.52	9.52	1.93	7.59	0.28	2.9
C	10.13	7.55	34.19	9.66	1.65	8.00	0.14	1.4

Table 3. Evaluation of tensile properties

Compound	Tensile strength, N mm^{-3}	Elongation, %	Modulus 100%, N mm^{-3}	Modulus 300%, N mm^{-3}
A	16.09	542.53	2.36	7.75
B	14.07	491.54	2.35	7.71
C	17.65	504.53	2.76	9.50

compound C is less than that of compound A and B. The reversion behavior depends on the network structure of the vulcanizates. Probably, the presence of phenyl groups in CSC[4]A–SiO$_2$ causes CSC[4]A–SiO$_2$ to act as an anti-reversion agent. During reversion, synchronously with the breakdown of polysulfide links, new type of crosslinks is formed based on Diels–Alder reaction and it prevents a decrease in the crosslink density. These new crosslinks have larger thermal stability and elasticity [27].

Tensile properties. Evaluation of tensile properties such as tensile strength, elongation at break and modulus (M100 and M300) of vulcanizates are given in Table 3 and fatigue resistance, hardness, and resilience are shown in Figs. 4a, 4b, and 4c, respectively.

Tensile strength and modulus depend on crosslink density of composite and are increased with increasing maximum torque. The tensile results (Table 3) show that the highest reinforcement is related to compound C, due to increased crosslink density in this compound, based on curing data these results were expected. The elongation at break indicates the elasticity of polymer, which is approximately the same in compound C and B, but less than in compound A. The increase in the crosslink density reduces the mobility of the polymer chains, resulting in a reduction in the elongation at break and an increase in hardness.

As Fig. 4b and Table 3 show that with increasing the crosslinks density in compound B and C hardness is improved and elongation at break decreases. Resilience
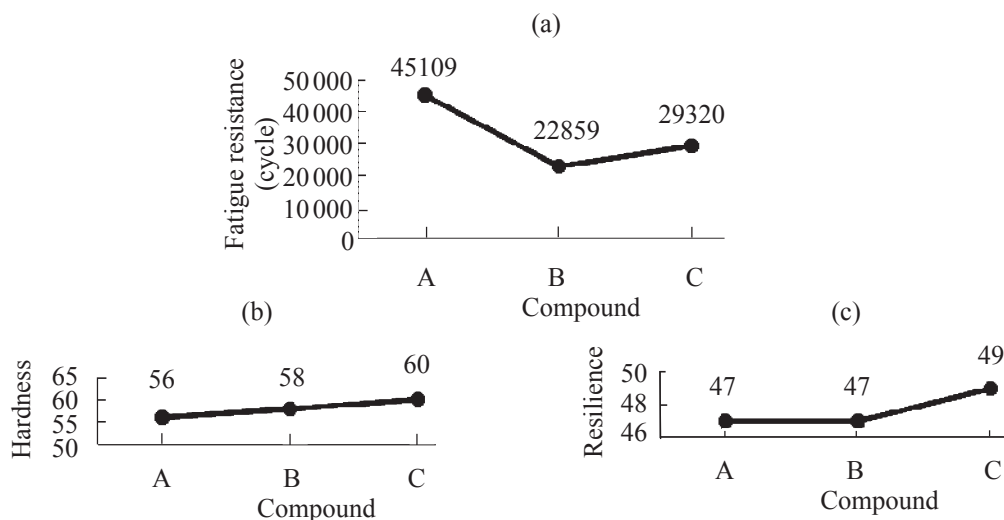
Fig. 4. (a) Fatigue resistance, (b) hardness, (c) resilience.

is another mechanical characteristic, which depends on crosslink density [28–31]. Increased resilience in compound C is associated with a 5% increasing in crosslink density in this compound.

According to an information in the literature, it is clear that fatigue resistance depends on polysulfide crosslinks [32]. In compounds with the same formulation, decrease in polysulfide crosslinks caused to decrease in fatigue resistance (decrease in the number of the cycle) [33]. Therefore as Fig. 4a shows, the behavior of compound C in terms of fatigue resistance (in other words, the concentration of polysulfide crosslinks) is better than that of the typical silica–silane system and even it shows improvement of up to 22% compared with that of the compound with silane.

CONCLUSIONS

As a summary in this study, a novel reinforcement filler (CSC[4]A–SiO$_2$) was synthesized and used in NR/BR blend based rubber compounds. The results indicated that the use of CSC[4]A–SiO$_2$ in addition to the reinforcing properties would produce a homogeneous and uniform surface. Importunately, the mechanical properties of compound in the presence of CSC[4]A–SiO$_2$ were improved dramatically especially relative to fatigue resistance. Furthermore, CSC[4]A–SiO$_2$ can acts as an anti-reversion agent and greatly reduces the reversion.

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CONFLICT OF INTEREST

The authors declare the absence of a conflict of interest that requires disclosure in this article.

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