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Scientific paper

Synthesis and Application of Silica Supported Calix[4]arene Derivative as a New Processing Aid Agent for Reducing Hysteresis of Tread Rubber Compounds Used in Low Rolling Resistance Tires

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Abstract

Rolling resistance is one of the most important properties of a tire which is highly dependent on the viscoelastic properties of its rubber compounds. There are a lot of ways to reduce this parameter both in construction improvement of the tire and changing in rubber compound formulation especially in tire tread formulation. Rubber scientists have been trying to introduce new processing aid agents beyond the traditional tire components for reducing the rolling resistance. In this study, a unique structure of silica-supported calix[4]arene (SS-CSC[4]A) has been synthesized and applied as a processing aid agent in tire tread formulation. Fourier-transform infrared spectroscopy (FTIR), Nuclear Magnetic Resonance (^{1}HNMR and ^{13}CNMR), ^{29}Si CP/MAS spectroscopy, thermal gravimetric analysis (TGA), elemental analysis, and acid-base titration were used to characterize its structure. Scanning Electron Microscopy (SEM) use to investigate the effect of prepared material on qualification of filler dispersion in the rubber matrix. The viscoelastic properties of the prepared rubber compound were measured by Dynamic Mechanical Thermal Analysis (DMTA) which showed the great decrease in rolling resistance of rubber compound based on SS-CSC[4]A as a processing aid agent. The mechanical and rheological properties of obtained tread rubber compound measured by tensometer and MDR rheometer showed no sensible changes in these properties.

Keywords: Rolling resistance; tire tread compound; silica-supported calix[4]arene; dynamic mechanical thermal analysis; processing aid agent; wet grip.

1. Introduction

Styrene-butadiene rubbers (SBRs) are a group of synthetic elastomers which is a random copolymer of styrene and butadiene.[1] These rubbers have a huge contribution to the production of car tires[2] because of their unique properties especially excellent abrasion resistance and good aging stability.[3,4] It is notable that the ratio of styrene and butadiene has an important role in the properties of the final product in order to enhance the ecumenical properties of tread compound in a passenger car tire, SBR is normally blended with BR.

SBR and BR are used as elastomers because of their amorphous structures. The absence of crystalline structures in these polymers gives rise to the low mechanical properties which hinder their uses.[5] One of the most effective ways to improve the mechanical properties of these polymers is to prepare their compounds with the addition of fillers such as carbon black or silica.[6] Although, the addition of such a rigid additive to the SBR and BR blends can increase their mechanical strength, it can complicate the process ability, decrease the adhesion and rises the friction between the tires and the surface which results in the high rolling resistance, heat build-up and fuel consumption.[7,8]

As a best of our knowledge, high performance rubber tread is in high demand, for example, high wet skid resistance (WSR) and low rolling resistance, which is in line with the concept of "green tires".[9] Thus, it is necessary to find alternative processing aid agents for using in rubber compounds to reduce heat build-up, hysteresis and rolling resistance. Generally, the processing aid agents used in rubber industry are polymers with low molecular weight, resins, fatty acids, and other hydrocarbon compounds.[10] The processing aid agent is a material that will be improved process ability and will be reduced plasticity. C5 (aliphatic hydrocarbon resin) and C9 (aromatic hydrocarbon resin) can do as processing and reinforcing agents. SP-1068 (phenolic resin) acts as a tackifying resin that makes strong hydrocarbon bonds with the rubber compound. G90 (coumarone indene resin) also acts as a tackifier and processing aid agent and belongs to the highly polar groups of processing aid agents.

Recently, Song[11] has reported a silica-based processing aid agent, utilizing terpene phenol resin (TPR) which enhanced the mechanical and fatigue properties, Kukreja et al.[12] found that the addition of palm oil in an NBR rubber matrix improved the aging resistance and plasticizing efficiency, Asharf et al.[13] reported that poly (methyl methacrylate) (PMMA) compounds with palm oil exhibited enhanced mechanical properties. Veiga et al.[14] investigated the replacement of carbon black by silica-organosilane coupling agent system and the number of processing steps on the mechanical properties, rolling resistance, and wet grip of truck tire treads. Hua et al.[15] studied the effect of vinyl and phenyl group content on the physical, dynamic and mechanical properties of HVBR and SSBR. Mensah et al.[16] explored the physico-mechanical properties of variable rubber blends including epoxide natural rubber (ENR), polybutadiene rubber (BR), and solution polymerized styrene-butadiene rubber (SSBR) filled by silanized silica and carbon black mixtures.

Calix[n]arenes are basket-shaped (vase-shaped) macrocyclic or cyclic oligomers composed of repeating *para*-alkyl phenolic monomers linked by methylene bridges to form a hydrophobic cavity and are simply functionalized both at the upper rim and lower rim. These compounds are based on the hydroxyl alkylation products of aldehydes and phenols with a defined upper rim, lower rim and a central annulus.[17]

Taghvaei-Ganjali and colleagues employed calix[4]arenes and their derivatives in sensors,[18] construction of polyurethane foams,[19] membrane electrode,[20] improvement of mechanical properties and thermal stability of polyurethane composite[21] and removal agents for ions.[22] As other researchers have reported, calix[n]arene derivatives can be used as heterogeneous catalytic system,[23] binders[24] and for detection of tryptophan.[25]

Our research group studied the use of calix[4]arene derivatives as sorbent,[26] filler,[27] tackifier resin,[28] anti-reversion agent[29] in rubber industry. Li et al. investigated the effect of phenolic antioxidants based on calixarene on the antioxidative properties of natural rubber.[30] Malekzadeh et al.[31] studied the influence of a silane coupling agent based on calix[4]arene on the properties of nano-silica filled rubber compound. As could be seen, the possible influence of calix[n]arenes as a processing aid agent on tire tread performance has not been examined in present literatures.

In the present study, a novel calixarene silica based 5, 11, 13, 17-tetrahydroxy 25, 26, 27, 28-tetrakis[chlorosulfonyl]calix[4]arene-bonded silica gel (SS-CSC[4]A), has been synthesized and applied as a processing aid agent in BR/SBR based rubber compounds in order to decrease of heat build-up and hysteresis which leads to reduction of rolling resistance.

2. Experimental

2. 1. Materials

Emulsion polymerized styrene butadiene rubber (E-SBR1502) was provided by Takhte Jamshid Petrochemical Company (Iran) and high-cis polybutadiene rubber 96% (BR) was purchased from Arak Petrochemical Company (Iran). N-330 carbon black was supplied by Pars Company (Iran). Aromatic oil (290, dark brown) was purchased from Iranol Company (Iran). The Hydrocarbon Resin (C5) was provided by Lesco Chemical (China). *p*-tert-Butylphenol was purchased from Merck (Germany) and applied without any purification and another three types of resins (C9, G90 and SP1068) were supplied by Taizhou Huangyan Donghai Chemical Company (China). N-cyclohexyl-2-benzothiazole sulfonamide (CBS), 1, 3-Diphenylguanidine (DPG) and 2, 2, 4-trimethyl-1, 2-dihydroquinoline (TMQ) and sulfur were supplied by Taizhou Huangyan Donghai Chemical Company (China). N-isopropyl-N'-phenyl-p-phenylene (IPPD) was provided by Nocil (India). The silica (Ultrasil VN3) was purchased from Evonik Company (Germany). Bis[3-(triethoxysilyl)propyl]tetrasulfide (TESPT) was purchased from Shin-Etsu company (Japan). Stearic acid (PALMAC 1600) was supplied by Acidchem Company (Malaysia) and Zinc oxide (ZnO) was manufactured by Sepid Oxide Shokuhie Company (Iran). Paraffin wax was supplied by Behran Company (Iran). N-(cyclohexylthio) phethalimide (PVI) was purchased from Changde Dingyuan (China). Silica-supported calix[4]arene derivative was synthesized in our research group.[32] All analytical grades of the reagents and solvents used in this study were provided by Merck Company (Germany) and were analytical pure grades.

2. 2. Synthesis

Synthetic strategy for preparation of silica-supported calix[4]arene derivative (SS-CSC[4]A) according to our published papar[32] has been illustrated in Figure 1.

2. 2. 1. Synthesis of *p*-tert-Butyl calix[4]arene (1)

p-tert-Butyl calix[4]arene was synthesized according to previously described method by Gutsche and Iqbal.[33]

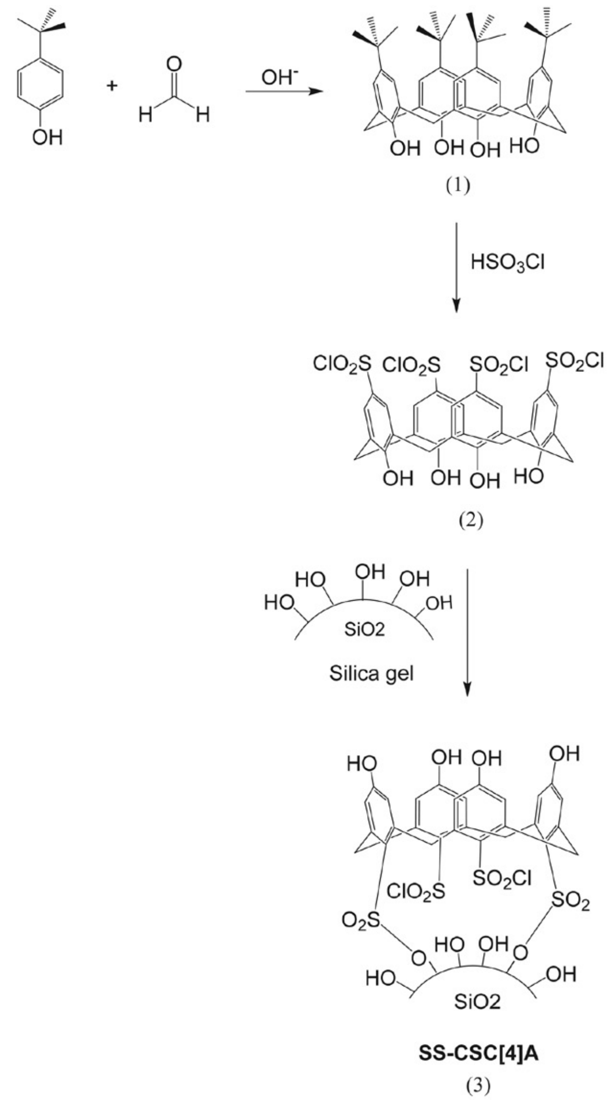

Figure 1. The synthetic strategy for silica-supported calix[4]arene.

Yield: 62%; mp: 342–344 °C; ATR-FTR: υ_{max} (cm^{-1}) = 3169, 2955, 1200, 1401; ^{1}H NMR (400 MHz, CDCl$_3$), δ(ppm): 1.21 (s, 36H, CH(CH$_3$)$_3$), 3.51 (d, 4H, ArCH$_2$Ar, *J* 12.8 Hz), 4.26 (d, 4H, ArCH$_2$Ar, *J* 12.8 Hz), 7.06 (s, 8H, Ar–H), 10.34 (s, 4H, OH); ^{13}C NMR: (100 MHz, CDCl$_3$), δ(ppm): 31.3, 32.4, 34.0, 126.2, 128.4, 144.5, 146.6.

2. 2. 2. Synthesis of Chlorosulfonyl-Calix[4]arene (2)

Chlorosulfonyl-Calix[4]arene (CSC[4]A) was prepared in accordance with a previous method described by Coquiere et al.[34] with some modification. A mixture of *p*-tert-butylcalix[4]arene (2 mmol) and dichloromethane (25 mL) was placed in a three necked 100 mL round-bottom flask equipped with a magnetic stirrer, reflux condenser and septum. The mixture was stirred for 15 min at room temperature in an inert atmosphere of nitrogen gas. Chlorosulfonic acid (5 mL) was slowly added by syringe at a rate to keep the temperature between 0 and 5 °C. When the addition of chlorosulfonic acid was finished, the solution mixture was refluxed for 2 h under vigorous stirring. After cooling, dry ether (30 mL) was added and the resulting oil after separating was triturated several times with methanol. CSC[4]A as a tan powder was given.

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$_6$, TMS), δ(ppm): 3.94 (8H, s, ArCH$_2$Ar), 7.39 (8H, s, Ar–H) and 11.39 (4H, s, 8OH); ^{13}C NMR: (125 MHz, DMSO-d$_6$), δ(ppm): 138.3 (ArC–SO$_2$), 30.4 (ArCH$_2$Ar); MS-FAB: m/z 817.0 (M$^+$, calcd 817.5)

2. 2. 3. Synthesis of Silica-Supported Calix[4]arene Derivative (SS-CSC[4]A) (3)

5 g of mesoporous silica gel was activated by refluxing with concentrated sulfuric acid and nitric acid [4:1] at 140 °C for 4 h to remove any adsorbed metal ions. The solution was filtered and obtained white powder was washed with distilled water until the neutral pH was gained. The residual solid was washed with acetone, methanol and dichloromethane, respectively and dried in an oven at 300 °C for 2 h to remove adsorbed surface water and maximize the number of silanol groups on the surface. Activated silica gel was put in a stream of dry nitrogen for 1 h and was used immediately.

100 mL round-bottom flask, equipped with a reflux condenser, a gas inlet tube for conducting of HCl gas over silver nitrate solution was used. It was charged with 50 mL anhydrous xylene, 1.5 g of activated silica gel and 1 g of CSC[4]A. The mixture was allowed to reflux under continuous stirring and a dry nitrogen atmosphere at 140 °C for 72 h. It was mentioned in order to prevent the crashing of silica gel particles and as a result changing the special surface area of silica particles during the reaction, the mechanical stirring was not used in this reaction. Instead, the stirring was done by bubbling of nitrogen gas over the reaction mixture. After carrying out the reaction, the suspension was vacuum filtered using a sintered glass funnel (porosity 3) and the residue was washed in sequence with dichloromethane (5 mL), diethyl ether (5 mL), methanol (5 mL) and hexane (5 mL). The unreacted CSC[4]A inside the pores of silica gel was extracted with acetone at reflux temperature for 12 h in a soxhlet system. The acetone solution was checked by thin layer chromatography and there was no evidence of unreacted CSC[4]A. The final product was dried in an oven at 150 °C for 12 h and kept in the desiccator.

SS-CSC[4]A was characterized by various physical techniques such as elemental analysis for C and Si, ATR-FTIR spectra for functional group confirmation, TGA for confirmation of covalently anchored organic groups and Solid-State ^{29}Si CP/MAS (cross-polarization/magic-angle spinning) NMR for the conformation of chemically bonding between silica gel and CSC[4]A.

Table 1. The results of elemental analysis and titration of SS-CSC[4]A.

Compound	**Elemental analysis**				**Titration**
	%C	**%H**	**%S**	**Bonded amount (μmol/g)**	**Acid capacity (mmol H^+/g)**
SS-CSC[4]A	3.11	0.45	1.15	92.82	0.17

The percentage of carbon, sulfur, hydrogen which was obtained from elemental analysis and resulting acidic properties of SS-CSC[4]A are given in Table 1. The carbon and sulfur contents were assigned to the loading of CSC[4]A over silica gel. The bonded amount was found to be 92.82 μmol/g (0.219 μmol/m^2) according to the carbon content shown in Table 1. Further, the sulfur content of SS-CSC[4]A was 0.36 mmol/g. The number of H^+ determined by acid-base titration was 0.17 mmol/g in the hydrolyzed sample. This value is half of the sulfur content, indicating that only two ester units took place onto SS-CSC[4]A and two acidic sites exist on the surface.

The TGA curve of SS-CSC[4]A shows two distinct stages of weight loss. The first weight loss is between 30 °C and 130 °C is attributed to the physically adsorbed water.[35] The second weight loss is observed between 160 °C and 900 °C which can be related to the decomposition of calixarene, corresponding to 92.82 μmol of CSC[4]A content per gram of silica.

FT-IR spectra were taken for a bare silica gel, CSC[4]A and SS-CSC[4]A. The major peaks of bare silica gel spectrum are: (a) a large broad band between 3200 and 3400 cm^{-1} attributed to the presence of the OH stretching frequency of the surface silanol group and adsorbed water (b) an intense peak at 1000–1250 cm^{-1} related to the antisymmetric Si–O–Si (siloxane) stretching in the amorphous silica (c) a band near 800 cm^{-1} is associated with the symmetric Si–O–Si stretching (d) a peak in the region 1600–1650 cm^{-1} is due to the bending mode of associated water molecules (e) the appearance of a peak at 900 cm^{-1} is related to Si–OH bending frequency. The infrared spectrum of the SS-CSC[4]A presented the same set of bands related to the silica gel, however some additional bands at 2883, 2827, 1457, 1936 and 650 which are assigned to the methylene asymmetric stretching, methylene symmetric stretching, C–H bending mode, benzene ring and C–S stretching mode respectively. Also, the appearance of the several peaks in the region between 1000 and 1500 cm^{-1} is a characteristic adsorption band of calixarenes. So, It is possible that the characteristic peaks of S=O group in compound SS-CSC[4]A which can be seen at 950–1040 cm^{-1}, overlapped with the strong broad band of siloxane in the compound SS-CSC[4]A. It is reasonable to mention here, because of the intense and broad band of siloxane in the region 1100 cm^{-1}, the intensities of the other bands in the spectrum are relatively small. To clarify the spectrum between 1200 and 4000 cm^{-1}, it was scaled up and magnified to show the differences more clearly. Considering the possible heterogeneity in the thickness of samples and the changes in the infrared beam positions, the band area of Si–OH bending frequency at 900 cm^{-1} after and before immobilization were calculated using the silica band at 1100 cm^{-1} as a reference band. The decrease of absorbance in the 900 cm^{-1} band region of SS-CSC[4]A in comparison with the spectrum of bare silica gel indicates that the Si–O–H vibration was affected due to the immobilization. These results which are obtained from IR spectrum are closely in agreement with published data.[36–38]

Direct evidence for chemical attachment of macrocyclic functionalized CSC[4]A to silica surface was done by ^{29}Si CP/MAS solid state NMR. Normally, the spectra of the bare silica gel shows three resonance peaks at −90, −100 and −110 ppm correspond to germinal silanol ($Si(OH)_2$, Q^2), free silanol (SiOH, Q^3) and siloxane (SiOSi, Q^4) respectively.[39] Because the resolution of the spectra is not sufficient to distinguish these signals, only one broad band was seen in the spectra. As a result of the introduction of functionalized calixarenes, the cross polarized ^{29}Si-MAS NMR spectra displayed unsymmetrical pattern when compared to the bare silica material.[40, 41] These results indicated the covalent-attachment of organic groups on the silica surface.

2. 3. Preparation of Rubber Compounds

In this study, seven tire tread compounds were prepared. The formulations of compounds are shown in Table 2. All compounds were mixed on a two-roll mill (Hiva Machinery Company, Iran) according to ASTM D3182 and vulcanization were done in 160 °C.

2. 4. Characterization

2. 4. 1. Cure Characteristics

Cure properties of tire tread compounds including scorch time (ts_2), cure time (tc_{90}), minimum torque (ML), maximum torque (MH) and cure rate index (CRI) were measured at 160 °C by a Moving Die Rheometer (MDR 2000) made by HIWA company according to ASTM D5289 standard. The curing characteristics of compounds have been shown in Table 3.

2. 4. 2. Mechanical Properties

The mechanical properties of prepared compounds including tensile strength, stress at 100% elongation

Table 2. Tire Tread Compound Formulations.

Ingredient	Component content (phr*)						
	A	**B**	**C**	**D**	**E**	**F**	**G**
BR	30	30	30	30	30	30	30
SBR	70	70	70	70	70	70	70
Carbon Black N330	45	45	45	45	45	45	45
Silica	20	20	20	20	20	20	20
Silane (TESPT)	1	1	1	1	1	1	1
ZnO	3	3	3	3	3	3	3
Stearic acid	2	2	2	2	2	2	2
Sulfur	1.6	1.6	1.6	1.6	1.6	1.6	1.6
P.Wax	2	2	2	2	2	2	2
IPPD	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TMQ	1	1	1	1	1	1	1
Aromatic oil	37	37	37	37	37	37	37
CBS	1.4	1.4	1.4	1.4	1.4	1.4	1.4
DPG	2	2	2	2	2	2	2
PVI	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Aliphatic hydrocarbon Resins (C5)	–	2	–	–	–	–	–
Aromatic hydrocarbon Resins (C9)	–	–	2	–	–	–	–
Coumarone Indene Resin (G90)	–	–	–	2	–	–	–
Phenolic Tackifying Resin (SP1068)	–	–	–	–	2	–	–
Para tert butyl phenol	–	–	–	–	–	2	–
SS-CSC[4]A	–	–	–	–	–	–	2

*phr represented the mass parts per 100 mass parts of BR/SBR blend.

Table 3. The results of curing behavior of rubber compounds.

Sample	ML (dN.m)	MH (dN.m)	MH-ML (dN.m)	Tc_{90} (Min)	T_{S2} (Min)	CRI (Min^{-1})
A	1.343 ± 0.213	7.570 ± 0.121	6.227 ± 0.234	13.672 ± 0.223	7.06 ± 0.211	15.125 ± 0.444
B	1.655 ± 0.111	8.277 ± 0.154	6.621 ± 0.054	14.721 ± 0.358	7.729 ± 0.276	14.301 ± 0.591
C	1.655 ± 0.132	8.139 ± 0.148	6.483 ± 0.229	13.823 ± 0.311	7.203 ± 0.257	15.106 ± 0.213
D	1.655 ± 0.112	8.691 ± 0.076	7.035 ± 0.211	14.125 ± 0.298	6.967 ± 0.122	13.972 ± 0.274
E	1.793 ± 0.163	8.415 ± 0.181	6.621 ± 0.017	13.832 ± 0.301	6.767 ± 0.130	14.156 ± 0.479
F	1.793 ± 0.224	8.691 ± 0.159	6.897 ± 0.326	15.46 ± 0.388	7.667 ± 0.199	12.832 ± 0.395
G	1.793 ± 0.194	8.691 ± 0.271	6.897 ± 0.077	14.682 ± 0.390	7.428 ± 0.295	13.784 ±0.565

(M100), 300% elongation (M300), and elongation at break were measured by a Universal Testing Machine (model; M350-5kN, Testometric Company, UK) according to the ASTM D412 C test method. Dumbbell-shaped specimens (2 mm thickness, 25 mm width and 100 mm length) were cut from molded sheets. The average values of the measured quantities and their standard errors were reported in Table 4.

Table 4. The results of mechanical properties of rubber compounds.

Sample	Processing aid agent	Tensile strength (MPa)	Elongation at break (%)	Modulus @ 100% (MPa)	Modulus @ 300% (MPa)
A	Blank	13.179 ± 0.876	647.693 ± 28.251	1.742 ± 0.027	5.042 ± 0.038
B	C5	13.227 ± 0.726	725.75 ± 24.344	1.493 ± 0.056	4.273 ± 0.096
C	C9	14.251 ± 0.44	746.179 ± 4.855	1.529 ± 0.085	4.436 ± 0.158
D	G90	14.958 ± 0.252	736.452 ± 4.583	1.729 ± 0.045	4.897 ± 0.105
E	SP-1068	14.549 ± 0.13	754.237 ± 6.797	1.820 ± 0.053	4.824 ± 0.086
F	*P*-tert	13.897 ± 0.319	745.163 ± 38.728	1.564 ± 0.131	4.443 ± 0.300
G	SS-CSC[4]A	14.175 ± 0.306	712.71 ± 23.45	1.762 ± 0.109	4-927 ± 0.230

2. 4. 3. Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical thermal properties of tire tread compounds were examined by using a dynamic mechanical thermal analyzer (DMTA; Tritec-2000; England) at temperature range from −140 °C to 90 °C in tension mode deformation and a frequency of 1.0 Hz according to ASTM E1640. The results have been shown in Tables 5 and 6.

2. 4. 4. Scanning Electron Microscopy (SEM)

The degree of filler dispersion in compounds G and A (blank) was tested by scanning electron microscopy (SEM, Philips-XL 30, Netherlands) with an accelerating voltage of 25 kV. The samples were supper-coated with gold to increase their electric conductivity before the examination.

3. Results and Discussions

3. 1. Curing Characteristics

The cure properties that include scorch time (ts_2), optimum cure time (tc_{90}), maximum and minimum torque (MH and ML), the difference in torque (ΔM = MH-ML), and the cure rate index (CRI) of different tire tread compounds (A-G) are shown in Table 3.

These data show that there are no significant changes in cure properties of rubber compounds by changing in processing aid agents.

3. 2. Mechanical Properties

In order to investigate the mechanical properties, the results of tensile strength, elongation at break, modulus at 100% and modulus at 300% after optimum vulcanization can be seen in Table 4.

The results of mechanical properties of rubber compounds A-G show that SS-CSC[4]A acts as C9 resins according to aromatic behavior and there are slightly increasing in tensile strength and elongation at break in comparison with blank compound A without any significant changes in modulus %100 and %300.

3. 3. DMTA

Dynamic mechanical thermal analysis (DMTA) of tire tread compounds due to prediction tire tread performance, mainly heat build-up, hysteresis and rolling resistance as an indicator of fuel consumption efficiency, is important in tire industry. For this purpose, the dependence of the loss factor (tan *δ*) on temperature at a constant frequency could be characterized. Therefore, the tan δ values at about 90 °C, 60 °C, 25 °C, 0 °C and −10 °C are used to predict heat build-up, rolling resistance, dry grip, wet grip and ice grip, respectively.[15, 42–50] The loss factor that is the ratio between the loss modulus to storage modulus (tan δ = E''/E'), is related to the macromolecule's movements and phase transition in the polymers.[50–52] The lower value of tan δ at 60 °C, 90 °C causes lower hysteresis (lower rolling resistance) and lower heat build-up, and therefore lower fuel consumption efficiency (The main mechanism of en-

Table 5. The results of dynamic mechanical thermal properties of rubber compounds A-G.

Sample	Processing aid agent	Tg (°C)	Tan δ (max)	E'_G (MPa)	E'_R (MPa)	E' 30 °C (MPa)	CLD (mol/m^2)
A	Blank	−44.2	2.64E + 03	0.5328	3.134	10.31	0.3466
B	C5	−44.5	2.68E + 03	0.5369	4.622	10.53	0.5112
C	C9	−44.0	2.69E + 03	0.5505	5.841	10.71	0.6460
D	G90	−40.8	2.29E + 03	0.5116	4.876	11.27	0.5393
E	SP-1068	−43.9	2.61E + 03	0.4891	7.498	15.89	0.8293
F	*P*-tert	−44.0	2.44E + 03	0.5188	5.030	10.87	0.5563
G	SS-CSC[4]A	−44.3	2.73E + 03	0.5324	5.421	11.31	0.5990

Table 6. tan δ at various temperature for compounds A-G derived by DMTA.

Sample	Processing aid agent	tan δ @ 90 °C	tan δ @ 60 °C	tan δ @ 25 °C	tan δ @ 0 °C	tan δ @ −10 °C
A	Blank	0.1627	0.1517	0.1668	0.1735	0.1773
B	C5	0.1378	0.1359	0.1564	0.1681	0.1746
C	C9	0.0922	0.1079	0.1413	0.1648	0.1739
D	G90	0.1321	0.1460	0.1615	0.1741	0.1797
E	SP-1068	0.1357	0.1512	0.1590	0.1672	0.1694
F	*P*-tert	0.1243	0.1326	0.1571	0.1717	0.1760
G	SS-CSC[4]A	0.1068	0.1176	0.1441	0.1549	0.1646

ergy loss in tread compound in a rolling tire is the Payne effect which has not been studied here).

On the other hand, the higher value of tan δ at low temperatures (–10 °C, 0 °C, 25 °C) indicates better grip properties of tire on the roads surface.[53,54] Figures 2–4 and Tables 5–6 represent the influence of different processing aid agents on tire tread performance and dynamic properties for tire tread compounds A-G.

As shown in Figure 3 and Table 5, C and E compounds had the highest and the lowest values of tan δ_{max} (peak of the tan δ). The almost same values of tan δ_{max} for the G and the blank compounds demonstrate that the amount of rubber chains participating in the glass transition for both compounds is in the same order.[55] Regarding this fact the value of E’ at 30 °C directly relates to the dry handling property of a tire[56], the highest value of E’ at 30 °C for the E compound indicates that the compound possessed the best dry handling property. The E’ value at 30 °C for the G compound increased about 9.7% compared to the obtained parameter for the blank compound. The value of cross-linking density (CLD) parameter in Equation (1) was obtained by the following equation[55]:

$$CLD = E'/3RT \qquad (1)$$

where E’, R, and T are corresponded to the minimum storage modules, the universal gas constant, and the absolute temperature at the rubbery plateau zone, respectively.

Based on Equation (1), the higher value of E’ at the rubbery region results in a higher degree of cross linking density. Therefore, from Table 5 it can be clearly seen that the E compound possessed the highest modulus at rubbery and so the highest degree of cross linking density. The higher E’ value at the rubbery zone for the G compound compared to the blank compound led to the increment of the cross linking density (about 72.8%) for the SS-CSC[4]A containing compound. The value of E’ at the glassy region for the G compound is the highest in comparison with other compounds and was about 3.4% more than the blank compound indicating the stronger structural interactions of SS-CSC[4]A in G compound with the matrix.

T_g is another parameter that can be obtained from the DMTA analysis. As can be seen, the lowest and highest values of T_g respectively belong to the B and E compounds. The T_g of tire tread compound decreases from –44.2 °C to –44.3 °C when there is SS-CSC[4]A. To understand the reason, the SS-CSC[4]A structure and its effect on silica particle dispersion have been studied. SS-CSC[4]A is a calixarene, that its cavity can relieve the force on itself by moving its flexible bonds, then it is accepted that when SS-CSC[4]A is added as mobile macromolecule to compound with cured chain, T_g must be decreased. On other hand, the addition of SS-CSC[4]A to compound provides better silica dispersion and more interaction between rubber chain and silica particle, which means we have to provide more energy for chain movement and this energy must be provided by higher temperature. According to the results, there is a trade-off between increasing and decreasing T_g when SS-CSC[4]A is added to compound, DMTA results show just 0.1 °C decrease in T_g, so the SS-CSC[4]A flexible bonds is the T_g controller.

In general, it is expected that with a gradual decrease in T_g, the values of tan δ will be increased. But as can be seen in results, tan δ values are lower than the blank compound at all temperatures in the presence of SS-CSC[4]A. At high temperature when it is well above T_g, the movement of the chains is very fast and long range. Regardless of the flexible structure, with the presence of SS-CSC[4]A as an external factor makes it difficult to move the polymer chain, so tan δ values were decreased.

According to Figure 4 and Table 6, the values of tan δ at 60 °C and 90 °C of compound G are decreased compared to blank compound (A), where the rolling resistance and heat build-up decreased by 22.5% and 34.4%, respectively. Which means the fuel consumption efficiency and heat build-up performance of compound G containing SS-CSC[4]A are improved. The fuel consumption of a passenger car will be reduced by 1–2% if the rolling resistance of tire is reduced by 10%, according to the literatures.[57–59]

But at lower temperature due to better dispersion of the silica particle and more interaction between matrix and filler, increasing of tan delta for silica filled in comparison to CB based compounds are mainly due to the higher polymer volume fraction in them. In fact, at a lower temperature, due to increase in stiffness of filler agglomerate and cluster, the release of occluded rubber is more difficult than the higher temperature. As in the case of silica compound, we have lower values of occluded rubber and thus polymer volume fraction is higher than CB compounds. As a result, tan δ values and grip decrease in G compound compared to blank compound.

Consequently, the use of SS-CSC[4]A as a processing aid agent in tire tread compounds, is beneficial for reduc-

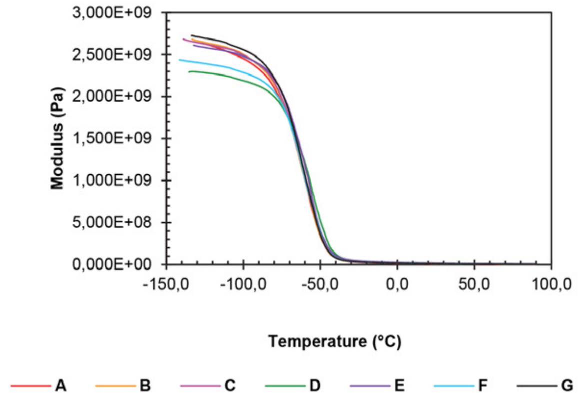

Figure 2. Storage modulus (E’) versus temperature curves of rubber samples containing various processing aid agent.

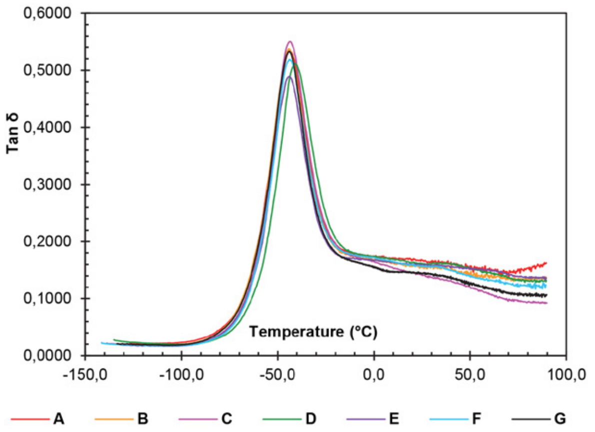

Figure 3. Loss factor (tan δ) versus temperature curves of rubber samples containing various processing aid agent.

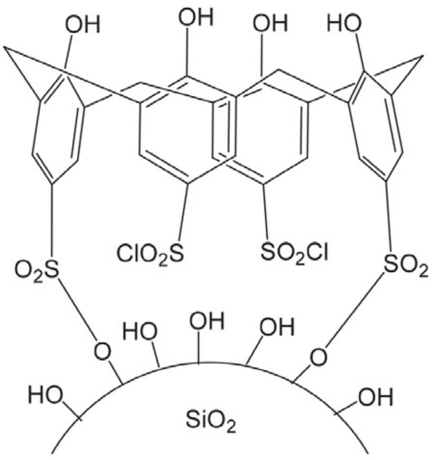

Figure 5. SS-CSC[4]A molecular structure.

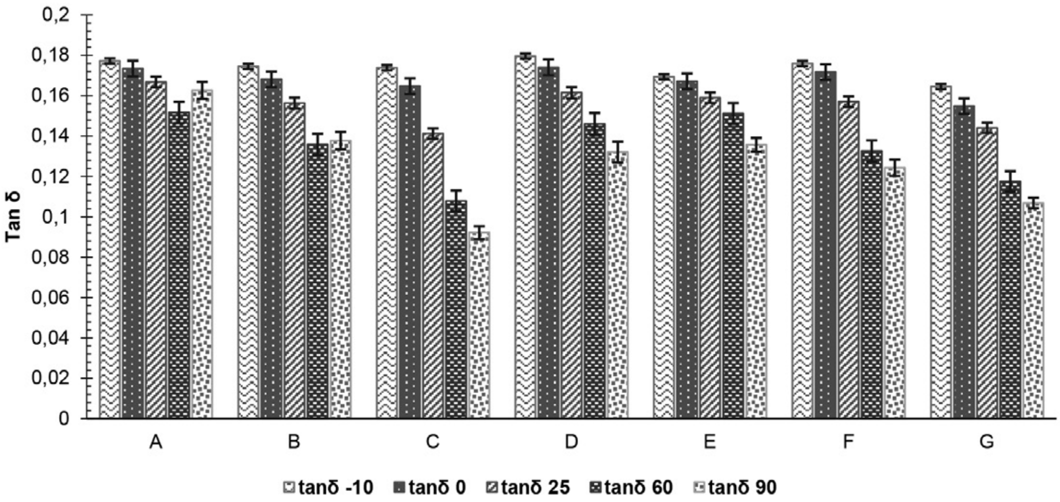

Figure 4. Loss factor (tan δ) values at different temperature of rubber samples containing various processing aid agent.

ing heat build-up, hysteresis and rolling resistance. This is because of better filler dispersion, stronger rubber-filler interaction, higher crosslink density and lower filler-filler interaction.

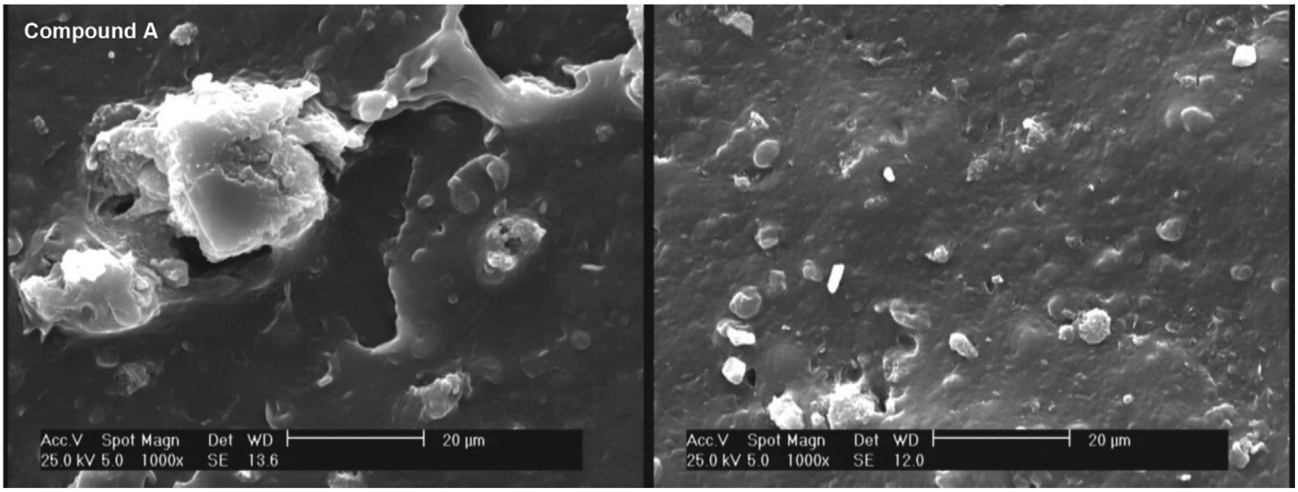

Figure 6. SEM images of compounds A and G.

3. 4. SEM Analysis

For investigating of the SS-CSC[4]A effect on silica dispersion in the rubber compound, the SEM analysis was done in compounds A (Blank) and G (SS-CSC[4]A) as a processing aid agent, are shown in Figure 6. As can be seen the presence of SS-CSC[4]A lead to better dispersion of silica particle in the rubber matrix.

According to the structure of SS-CSC[4]A, there is dual structural behavior. A fair dispersity to the silica as filler via lower rim silica-supported moiety and good physical connection to rubber matrix via upper rim moiety of aromatic based calixarene. As a result, better silica disperses is observed in the rubber matrix in the presence of SS-CSC[4]A as dispersing agents.

4. Conclusion

In this study in order for improvement of rolling resistance and heat build-up of tire tread compound a unique processing aid agent, SS-CSC[4]A was synthesized. FTIR and NMR proved the structure of SS-CSC[4]A. DMTA results showed a reduction in rolling resistance (22.5%) and heat build-up (34.4%), due to the effect of SS-CSC[4]A on silica dispersion and interaction between matrix and filler. SEM results showed a great silica dispersion when there is SS-CSC[4]A in the compound, and the tensile test did not illustrate any tangible changes for the compound containing SS-CSC[4]A. On the other hand, cure properties showed a slight increase in cure parameters because of the interaction enhancement between uncured polymeric chain, filler and macromolecule SS-CSC[4]A.

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Povzetek

Kotalni upor (ang. rolling resistance) je ena najpomembnejših lastnosti pnevmatik, ki je zelo odvisna od viskoelastičnih lastnosti njenih komponent. Obstaja več načinov za zmanjšanje tega parametra, tako s samo konstrukcijo pnevmatike kot tudi s spreminjanjem njene sestave, še posebej pri načrtovanju profilnega dela. Raziskovalci na tem področju zato poskušajo z uvajanjem novih aditivov, ki bi zmanjšali kotalni upor. V tej študiji smo na silikatno osnovo sintetizirali derivat kaliks[4]arena (SS-CSC[4]A) edinstvene strukture in ga uporabili kot polnilo profilnega dela pnevmatik. FTIR, magnetno resonanco (^{1}HNMR and ^{13}CNMR), ^{29}Si CP/MAS spektroskopijo, termično gravimetrično analizo (TGA), elementno analizo in titracijo smo uporabili za karakterizacijo. Učinkovitosti dispergiranja polnila v gumi smo določili z vrstično elektronsko mikroskopijo (SEM). Viskoelastične lastnosti tako pripravljene gume smo izmerili z dinamično mehanično termično analizo (DMTA), ki je pokazala znatno zmanjšanje kotalnega upora v primerjave z gumo brez SS-CSC[4]A polnila. Meritve opravljene s tenzometrom in MDR reometrom pa niso pokazale drugih bistvenih razlik mehanskih in reoloških lastnosti.