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Thermal stability of CR/CSM rubber blends filled with nano- and micro-silica particles

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Abstract The properties of filled polymers depend on the properties of the matrix and the filler, the concentration of the components and their interactions. In this research we investigated the rheological and mechanical properties and thermal stability of polychloroprene/chlorosulfonated polyethylene (CR/CSM) rubber blends filled with nano- and micro-silica particles. The density of the nano-silica filled CR/CSM rubber blends was lower than that of the micro-silica filled samples but the tensile strength and elongation at break were much higher. The nano-silica filled CR/CSM rubber blend has higher V_{r0}/V_{rf} values than micro-silica composites and show better polymer–filler interaction according to Kraus equation. The nano-silica filled CR/CSM rubber blends were transparent at all filler concentration, and have higher glass transition values than micro-silica filled compounds. The higher values of the glass transition temperatures for the nano- than the micro-filled cross-linked systems are indicated by DMA analysis. The nano-filled cross-linked systems have a larger number of SiO–C links than micro-filled cross-linked systems and hence increased stability.

Keywords Nano- and micro-silica filler · Polychloroprene/chlorosulfonated polyethylene (CR/CSM) rubber blends · Thermal stability

Introduction

Modern engineering systems are being increasingly produced from components that combine two or more materials for enhanced performance. During the processing of rubber vulcanizates, mixing of filler and cross linking are the two substantial parameters as the homogeneity of mixing and cross linking significantly affect the properties of the vulcanizates. Recent investigations (from both a technological and fundamental point of view) show that the interfacial bonding strength has a profound influence on the failure of dissimilar or composite materials [1]. Silica has been used as non-black reinforcing filler in the rubber industry for a long time. Reinforced rubber blends are suitable materials for industrial practice [2]. Obviously, in such systems both components (filler and rubber) have the reactive groups for the additional cross linking reaction to take place [3]. Besides the so-called "dispersion" forces there are a variety of other interactions between particles. A key one among them is hydrogen bonding, which tends to be a significant force in the case of fumed silica, where hydrogen bonding between surface silanol groups takes place. Many authors have investigated the role of filler networking in the elastic properties of elastomer composites [4]. The surface of hydrated or precipitated silica is highly polar and hydrophilic because of the presence of numerous silanol groups. The evaluation of the reinforcing effect is usually based on the determination of the processability of elastomers, and the dynamic mechanical properties of cross linked materials [5]. In this work the effect of nano- and micro-silica on mechanical properties and thermal stability of matrix blend based on polychloroprene and chlorosulfonated polyethylene (CR/CSM) rubber was studied.

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Experimental

Materials

All mixing ingredients were used as received. Rubbers used for composite preparation: Polychloroprene rubber, Baypren 110 from Bayer, Germany, ($\rho = 1{,}23$ g/cm^{3}ML 1 + 4/100 °C, 44-54); Chlorosulfonated polyethylene rubber, Hypalon 40S, produced by Goodrich Chemical Co. ($\rho = 1{,}18$ g/cm^3, Mw 5,52x10^5, Mw/Mn 1.97). Filler: active precipitated nano-silica, Ultrasil VN$_3$ (BET 160-200 (N$_2$) m^2/g, DBP absorption 220 cm^3/100 g) with the average size of primary particle 15 nm; micro-silica, diatomaceous earth, Celite 281 (DBP absorption 130 cm^3/100 g) with the average size of primary particle 28 μm (Table 1). The other rubber ingredients were: naphthenic oil (Tephil Naphtene P.O.100), stearic acid, and zinc oxide (ZnO) obtained from Bayer; sulfur (S) obtained from Chemmin Corporation, magnesium oxide (Anscor P), ethylene thiourea (ETU), very fast accelerator tetra methyl thiuram disulfide (TMTD), and slow accelerator N-cyclohexyl-2-benzothiazole sulfonamide (Vulcanite CZ). For efficient vulcanization (EV) system, the amounts of TMTD and S were 2.5 and 0.75 phr (parts per hundred), respectively.

Methods of preparations

The rubber compounds (Table 2) were prepared by using a laboratory-size two-roll mill maintained at 40 ± 5 °C. The roller speed ratio was $n_1/n_2 = 28/22$. The mixing time was 20 min. After mixing, the Mooney viscosity (ML 1 + 4 at 100 °C) of the compounds was measured by a Mooney viscometer. The sheeted rubber compound was conditioned at 23 ± 2 °C for 24 h prior to cure assessment on a Monsanto Moving Die Rheometer (model 100S) at 160 °C. The compound formulations (Table 2) expressed in part per hundred parts of rubber, phr. All test specimens were compression molded at 160 °C during the respective optimum cure time (t_{c90}) determined from the Monsanto Rheometer.

Methods of characterization

Rheometric characteristic

The cure characteristics: M_l (minimum torque), M_h (maximum torque), t_{c90} (optimum cure time), t_{s2} (scorch time) and CRI (cure rate index) were determined with a Monsanto Rheometer model 100S at 160 °C in accordance with ASTM method D-2084.

Table 1 Analytical data for the fillers

Filler	BET (N$_2$)/ m^{2}g^{-1}	DBP absorption/ cm^{3}100 g^{-1}	pH	Particle size
Nano-silica	160–200	220	6.7	15 nm
Micro-silica	–	130	10	28 μm

Table 2 Formulation of the compounds based on unfilled and nano- and micro-silica particle sized filled polychloroprene (CR) and chlorosulfonated polyethylene (CSM) rubber blends

Compounds/phr[a]	1	2	3	4	5	6	7
CSM	50	50	50	50	50	50	50
CR	50	50	50	50	50	50	50
ZnO	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Stearic acid	2	2	2	2	2	2	2
Nano-silica	0	10	20	35	0	0	0
Micro-silica	0	0	0	0	10	20	35
Naphthenic oil	0	3.3	6.7	11	3.3	6.7	11
MgO	2	2	2	2	2	2	2
ETU	0.5	0.5	0.5	0.5	0.5	0.5	0.5
TMTD	1	1	1	1	1	1	1
S	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Diethylene glycol	0	0.3	0.7	1.1	0.3	0.7	1.1

[a] Part per hundred rubber

Fourier transform infrared spectra (FTIR-ATR)

Fourier transform infrared spectra (FTIR) were recorded on a Bruker IFS-66 spectrometer with an attenuated total reflection (ATR) attachment. The internal reflection element (IRE) chosen was a 45-degree KRS-5. Samples for measurements were approximately 0.3 mm thick sheets, prepared by compression molding between two teflon films at temperature of 100 °C.

Measurement of mechanical properties

Tensile properties were measured at room temperature on an electric tensile testing machine (Zwick 1425) according to ASTM D 412. Hardness was measured using an indentation hardness tester according to ISO7619. The shear modulus, G, were obtained from the initial slope of the curve in Neo-Hook's stress–strain relation σ versus $(\alpha - \alpha^{-2})$ in equation:

$$\sigma = G(\alpha - \alpha^{-2}) \tag{1}$$

Dynamical mechanical analysis (DMA)

Dynamical mechanical properties were studied on a Mechanical analyzer Tritec 2000 (Triton Technology). Complex Young's modulus ($E^* = E' + iE''$, E' is a storage and E'' loss modulus) was measured in a single cantilever-bending mode. Temperature dependencies of dynamic mechanical properties were measured at a heating rate of 2 °C/min in the temperature range from −50 to 150 °C.

Multifrequency mode was used to determine a dependence of E^* on frequency (f) at frequency $f = 1$ Hz. Cross linking density can be obtained using DMA by calculating M_c, the (number) average molar mass of elastically effective chains (between cross links), according to the following equation derived from the theory of rubber elasticity [6]:

$$E = 3\rho RT/M_c \quad (2)$$

where E is the elastic modulus in the rubbery plateau (assimilated to the storage modulus E' measured at 1 Hz), R the gas constant, T the absolute temperature and ρ the material density at T.

Cross-linking density determination

The cross-link density of specimens was measured on the basis of the rapid solvent-swelling measurements (toluene uptake for 72 h at 25 °C) by applying the Flory–Rehner equation [7]. χ is the interaction coefficient between the rubber network and solvent (0.49) which is calculated by Eq. 3. The degree of cross link density (V) is given by Eq. 4

$$\chi = (\delta_s - \delta_r)V_0/RT \quad (3)$$

$$V = 1/(2M_c) \quad (4)$$

where δ_s and δ_r are the solubility parameters of the solvent and rubber network, respectively. R is the universal gas constant and T is the absolute temperature.

Filler–polymer interaction

The Kraus model [8] used for investigating the swelling of filler-reinforced vulcanizates, which shows how to calculate quantitatively the effect of particles either completely unbound, or completely and permanently bonded to the polymer. Kraus equation is

$$V_{r0}/V_{rf} = 1 - [m\phi/1 - \phi] \quad (5)$$

where

$$m = 3C(1 - V_{r0}^{1/3}) + V_{r0} - 1 \quad (6)$$

V_{r0} and V_{rf} are the volume fraction of unfilled and filled rubber blend, respectively; C is a constant characteristic of the filler but independent of the solvent and ϕ is the volume fraction of filler in the vulcanizates [9–12].

Thermal stability of the silica reinforced CR/CSM rubber blends

The thermal stability of pure CR/CSM rubber blend and (CR/CSM) rubber blends filled with nano- and micro-silica particles was investigated by non-isothermal thermogravimetric analysis (TG) using a Perkin Elmer TGS-2 instrument. The measurements were conducted at heating rates of 10 °C min^{-1} in a dynamic nitrogen atmosphere (flow rate 25 cm^3 min^{-1}), in the temperature range from 25 to 750 °C. The average sample mass was about 8 mg.

Results and discussions

Cure characteristics

The maximum and minimum torque (M_h and M_l) and delta torque (ΔM) at 160 °C (Table 3) increases with the increase of the nano- and micro-silica loading filler of the CR/CSM cross-linking systems. The difference between M_h and M_l could be used as an indirect indication of the cross-link density of the rubber compound [13]. Both scorch time (t_{S2}) and optimum curing time (t_{c90}) are found to decrease noticeably with increasing silica loading. The nano-silica particle size filled rubber blends have higher values than micro-silica particle size for all cure characteristics.

IR spectral analysis

ATR spectra carried out on samples of pure CR/CSM rubber blend and of two composites with two different silica particle size contents are displayed in Fig. 1 (spectrum 1, 2 and 3) The assignment of the principal bands is presented in Table 4.

Almost all bands [14] of the pure polymer blend especially those associated with the stretching bands of the CH_2 groups are shifted to lower wavenumbers in the filled polymer blend spectra. The bands located at 2943 and 2862 cm^{-1}, respectively, assigned to the asymmetric and symmetric stretch of the methylene group, are found at 2943 and 2860 cm^{-1} for the nano-silica filled CR/CSM composite and at 2926 and 2858 cm^{-1} for the micro-silica filled CR/CSM composite sample. The absorption band at 1108 cm^{-1} in the cross-linked CR/CSM rubber blend is assigned to symmetric vibration of SO_2 group. The peaks

Table 3 The cure characteristics of unfilled and nano- and micro-silica particle size filled CR/CSM compounds

Cure characteristics	Sample						
	1	2	3	4	5	6	7
M_h/daNm	38	34	41	47	37	34	39
M_l/daNm	8	10	11	13	8	8	8
ΔM/daNm	30	24	30	34	29	26	31
t_{S2}/min	2.32	3.25	3.13	2.38	2.14	1.59	1.39
t_{C90}/min	23.08	19.15	20.21	21.15	21.50	23.07	16.24

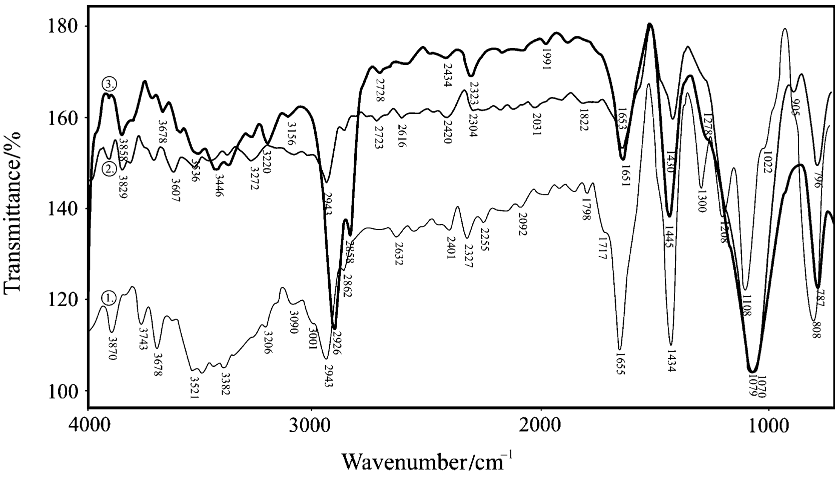


Fig. 1 FTIR-ATR spectrum of: (1) unfilled, (2) nano and (3) micro-silica particle size filled polychloroprene (CR) and chlorosulfonated polyethylene (CSM) rubber blends CR/CSM (50/50 w/w)

Table 4 FTIR-ATR spectroscopic data for unfilled and nano- and micro-silica particle size filled polychloroprene (CR) and chlorosulfonated polyethylene (CSM) rubber blends CR/CSM (50/50 w/w)

	Wave number/ cm^{-1}	Group	Assignment
CR/CSM (50/50 w/w) rubber blend	2943	CH_3–, –CH_2–,>CH–	ν (–C–H)
	2862	CH_3–, –CH_2–,>CH–	ν (–C–H)
	1655	–CH=CH–	ν (–C=C)
	1434	RHC=CHR	δ (–C–H)
	1108	–SO_2–	ν $(SO_2)_{sym.}$
CR/CSM/ Nanosilica rubber blend	2943	CH_3–, –CH_2–,>CH–	ν (–C–H)
	2860	CH_3–, –CH_2–,>CH–	ν (–C–H)
	1653	–CH=CH–	ν (–C=C)
	1430	RHC=CHR	δ (–C–H)
	1108	–SO_2–	ν $(SO_2)_{sym.}$
	1070	SiO–C	ν (SiO–C)
CR/CSM/ Microsilica rubber blend	2926	CH_3–, –CH_2–,>CH–	ν (–C–H)
	2858	CH_3–, –CH_2–,>CH–	ν (–C–H)
	1651	–CH=CH–	ν (–C=C)
	1445	RHC=CHR	δ (–C–H)
	1108	–SO_2–	ν $(SO_2)_{sym}$
	1079	SiO–C	ν (SiO–C)

ν Stretching vibrations, δ-bending vibrations in plain

of –S–Cl which is attributed to the–SO_2Cl group from CSM is absence, and the peak of –C–Cl from CR rubber is absence also. This suggests the cross linking of the rubber blend macromolecules. Similar observations were made by Ahankaria et al. [15] with reference to the thermally induced self-cross linking PVC/CR, as well as the PVC/CSM.

The absorption bands at 1655 and 1434 cm^{-1} in the cross-linked CR/CSM rubber blend are assigned, respectively, to symmetric and asymmetric bending vibration of C=C group. The weak absorption bands at 3536 and 3446 cm^{-1} which is attributed to hydrogen bands are strongly attenuated by reaction macromolecules and fillers. New absorption bands centered at 1070 and 1079 cm^{-1} could be assigned to the symmetric stretching modes of SiO–C group from silica filler, and moving symmetric and asymmetric bending vibration of C=C group from 1655–1651 to 1653 cm^{-1} and from 1434–1430 to 1445 cm^{-1} (Fig. 1, spectrum 2 and 3), suggests interaction of the polymers matrix with the silica, also.

Mechanical properties

Table 5 represents the effect of nano- and micro-silica loading on tensile properties (tensile strength, modulus and elongation at break) and hardness of the rubber vulkanizates. The tensile strength increases with increasing nano- and micro-silica loading in CR/CSM rubber compound. Maximum value of tensile strength, for nano-silica filled CR/CSM rubber compound is by sample 4 and 7 with 35 phr nano- and micro-silica (15.8 and 8.5 MPa). The improvement in tensile properties for nano-silica filled composites seems to be responsible for the improved dispersion of the nano-silica into the rubber matrix, leading to a higher bound rubber formation [16]. The values of 300% modulus are increase from 6.5 to 7.1 MPa for nano-silica and 2.8 to 3 MPa for micro-silica filled compounds,

Table 5 Some mechanical properties of unfilled and nano- and micro-silica particle size filled CR/CSM compounds

Characteristics	Sample						
	1	2	3	4	5	6	7
Tensile strength/MPa	6.4	13.6	14.6	15.8	6.6	8.3	8.5
Elongation at break/%	688	572	523	485	600	600	549
Hardness/shore A	57	65	69	71	55	55	55
Modulus at 300% elongation/ MPa	2.8	6.5	7	7.1	2.8	3	3

respectively. The hardness values of micro-silica filled compounds are the same and much lower than nano-silica filled compounds as shown in Table 5.

Values of elongation at break are decreasing with silica loading is increasing. The increase of hardness, modulus, and tensile strength and higher values for nano- than micro-silica composites can possibly be explained by the improvement of the degree of adhesion at interfaces between the nano-silica and the CR/CSM rubber blends.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) is based on differences in mechanical damping properties of unfilled and filled rubber vulcanizates [17]. Figure 2 and Table 6 show the elastic modulus, E', and tan δ determined from a dynamic mechanical analyzer under the conditions of 1 Hz and 0.1% dynamic strain amplitude. The addition of filler to rubber matrix would lower the peak value of tan δ, designated as (tan δ max), in the plot of tan δ versus temperature. E′ of blends increases significantly with addition of silica, particularly at a temperature above the CR/CSM rubber blend glass transition temperature (T_g). This result indicates a strong reinforcement caused by strong interaction between silica and CR/CSM rubber blend via silanol groups and chlorine atoms, respectively (Table 6) [18]. Values of glass transition temperature (T_g) determined from the damping peak tan δ are summarized in Table 6. In theory, the shift in T_g would be caused by silica–polymer interaction and/or a change in phase compatibility.

Cross-linking density

The values of R_W and R_V (Table 7) decrease with increasing amount of both nano- and micro-silica.

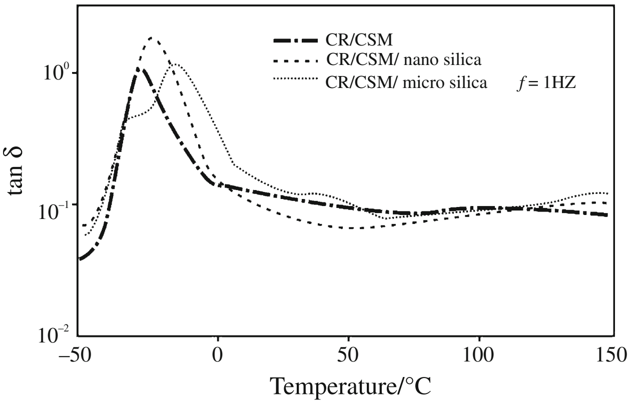


Fig. 2 Damping properties (tan δ) as a function of temperature of the unfilled and nano- and micro-silica particle size filled CR/CSM (50/50) rubber blend

Table 6 The glass transition temperatures (T_g) estimated either by dynamical spectroscopy (T_{gm}), the modulus of elasticity (G) determined from stress–strain measurement and crosslink density (v_e) calculated from the storage modulus E' (at 70 °C, 1 Hz) or (V) determined by swelling

Compounds	Sample		
	1	4	7
$T_{gm\ (1\ HZ)}$/°C	−21	−29	−16
G/MPa	6.4	15.8	8.5
E′/10^3MPa	5.2	18.1	7.5
V/mol m^{-3}	553	646	173
v_e/mol m^{-3}(from E′)	470	933	756

Table 7 The cross-linking density of unfilled and nano- and micro-silica particle size filled CR/CSM compounds

Parameters	Sample						
	1	2	3	4	5	6	7
ρ_p/g cm^{-3}	1.233	1.27	1.297	1.302	1.13	1.16	1.17
R_w	1.072	1.690	1.740	1.065	2.031	1.840	1.069
R_v	1.086	1.219	1.195	1.058	1.211	1.099	1.058
V/mol/m^3	553	231	430	646	391	242	173
M_c/g mol^{-1}	1115	2749	1580	1008	1621	2683	3884

The cross-linking density, V, increased with increasing silica concentration and was the largest for the sample containing nano- and micro-silica of 35 and 10 phr, respectively (samples 4 and 5). The largest chain molecular mass was obtained for micro-silica filled compounds with amount of 35 phr (sample 7) and the smallest for the sample 4 with the highest amount of nano-silica. The swelling degree decrease can be explained by linkage combination between polymer chains and functional groups on the silica surface, and by a possible increase in cross-linking bonds in the polymer matrix because of filler influence on the vulcanization reaction [19]. The cross link density (v_e) of the nano- and micro-silica particle size filled CR/CSM rubber blend was calculated from the equilibrium storage modulus in the rubber region over the α-relaxation temperature according to the rubber elasticity theory. The correlations of some data for the modulus of elasticity (G) determined from stress–strain measurement, and cross link density (v_e) calculated from the storage modulus E′ (at 70 °C, 1 Hz) or (V) determined by swelling are included in Table 6.

Figure 3 shows the plot of V_{r0}/V_{rf} versus $\phi/(1-\phi)$ according to Kraus equation [20]. It can be observed exhibit deviations from the proposed linear model, which are greater than 1. As filler loading increases, the ratio of

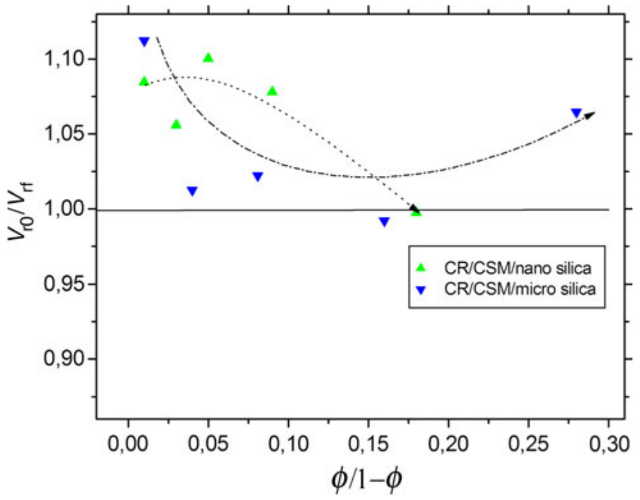


Fig. 3 Plot of V_{r0}/V_{rf} versus $\phi/(1-\phi)$ according to Kraus equation for swelling test of nano- and micro-silica particle size filled CR/CSM (50/50) rubber blend

V_{r0}/V_{rf} decreased. The nano-silica filled CR/CSM rubber blend has higher V_{r0}/V_{rf} values than micro-silica composites and show better polymer–filler interaction.

Thermal stability of CR/CSM compounds filled with nano- and micro-silica particle size

The thermal stability of pure CR/CSM rubber blend and CR/CSM rubber blends filled with nano- and micro-silica particles has been discussed. The thermal decomposition of CR/CSM rubber blend and nano- and micro-silica particle size filled CR/CSM rubber blends occur generally in two main stages (Fig. 4a, b; Table 8). The first-step degradation occurs in the temperature region 250–300 °C and the second-step degradation is about at 440 °C. The date for the initial decomposition temperature (IDT) (5% mass loss) [21], 10 and 30% mass loss temperatures are given in Table 8 and Fig. 4a. It can be seen that according to the IDT nano-silica filled CR/CSM compounds are more stability than unfilled and micro-silica filled compounds. In the next step (at 10% mass loss) with 20 phr of nano-silica and 30 phr of micro-silica particle size filled CR/CSM rubber have higher temperature values (262 and 259 °C) than other samples. At 30% mass loss, the CR/CSM rubber blends filled with 20 phr of nano-silica and 30 phr of micro-silica particle size are the most stability also, than other compounds.

Figure 4a, b shows that unfilled CR/CSM rubber blend compounds initially more stable than other samples. In the CR/CSM rubber blend compounds filled by nano- and micro-silica types (Table 8; Scheme 1) the degradation takes place in two stages. Up to 100 °C, there is no change and hence no mass loss. The first-step degradation occurs in the temperature region 250–350 °C and the mass loss in the range 21.15–27.93 and 21.15–28.76% (depending on the type and amount of silica in CR/CSM rubber blends) most probably indicating the evaporation of oil (naftolen). The second-step degradation starts at 440 °C and ends at 700 °C. The percent of mass loss at this region is in the range of 47.67–61.58 and 52.66–62.06% for nano- and micro-silica filled CR/CSM rubber blend indicating polymer degradation. The large flexible polysulfidic linkages undergo chain scission and convert into monosulfidic and disulfidic linkages. Synthetic rubber decomposes by random-chain scission with intramolecular hydrogen transfer. Table 8 presents the DTG peak values of CR/CSM rubber compounds filled by nano- and micro-silica particle size. The shift of values of the DTG peaks to a high temperature indicating increased thermal stability with 20 phr content of both nano-and micro-silica.

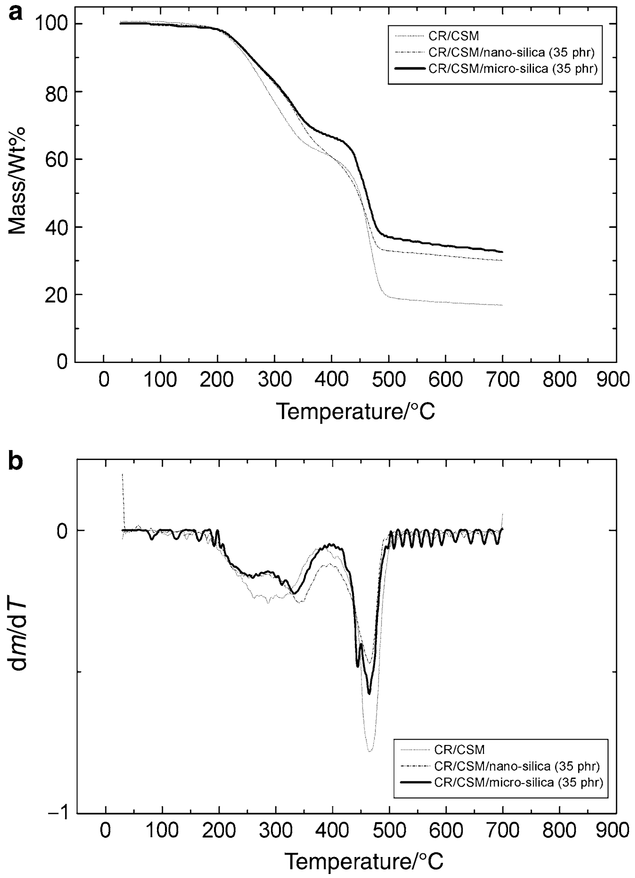
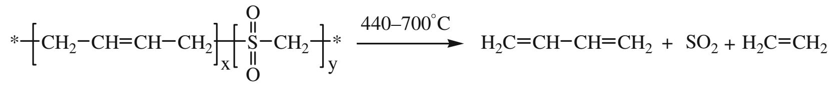


Fig. 4 **a** TG curves of unfilled and nano- and micro-silica particle size filled CR/CSM (50/50) rubber blend. **b** DTG curves of unfilled and nano- and micro-silica particle size filled CR/CSM (50/50) rubber blend

Table 8 The temperature values of unfilled and nano- and micro-silica particle size filled CR/CSM compounds for selected mass loss (5; 10 and 30%)

Compound	Sample						
	1	2	3	4	5	6	7
DTG peak values/°C	293.79	320.51	330.35	343.01	334.16	328.87	332.17
	464.64	447.77	468.15	465.34	461.21	469.81	464.51
Mass loss/%	21.15	26.86	25.44	27.93	28.76	25.67	24.36
	61.58	47.67	58.38	58.85	62.06	60.63	52.66
Total mass loss/%	84.01	75.73	71.57	69.91	77.52	73.59	67.17
Temperature values for selected mass loss							
$T_{5\%}$/°C	225.62	227.81	232.57	233.25	230.51	231.01	232.02
$T_{10\%}$/°C	251.61	241.77	262.16	256.3	247.39	254.42	258.64
$T_{30\%}$/°C	326.14	333.17	351.45	347.93	338.09	345.12	358.48



$$*\!-\!\left[CH_2-CH=CH-CH_2\right]_x\left[\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-CH_2\right]_y\!-\!* \xrightarrow{440\text{–}700^{\circ}C} H_2C=CH-CH=CH_2 + SO_2 + H_2C=CH_2$$

Scheme 1 Decomposition mechanism of CR/CSM rubber blend

Conclusions

This study illustrates the intrinsic potential of nano silica particle sized as reinforcing filler in elastomeric materials. The nano-silica filled CR/CSM rubber blends have higher values for cure characteristics than micro-silica particle sized filled compounds. Nano-silica type activated the vulcanizing process through the promotion of hydrogen sulfide formation and the rapture of S–N linkage when heated with sulfonamides in rubber either in the present or absence of other compounding ingredients. The strong peak from SiO–C at 1070 and 1079 cm^{-1} in the IR spectrum of nano- and micro-silica filled CR/CSM rubber blend suggested the presence of interaction with silica which lead to increased stability of the filled CR/CSM polymer blends. According to Kraus equation, it can be observed that the nano-silica filled CR/CSM rubber blend have higher V_{r0}/V_{rf} values and better rubber filler interactions than that micro-silica filled composites. The higher values of the glass transition temperatures for the nano- than the micro-filled cross-linked systems indicated by DMA analysis. The density of the nano-silica filled CR/CSM rubber blends was lower than that of the micro silica filled and were transparent at all filler concentration.

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