Improving properties of silicone rubber composites using macromolecular silane coupling agent (MMSCA)

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ABSTRACT: Two types of vinyl silicone oil (VSO), allyl-capped hyperbranched polycarbosilane (HBP), and triethoxysilane (TES) were employed to synthesize macromolecular silane coupling agent (MMSCA) by hydrosilylation. VSOs, HBP, and the hydrosilylated products were used as crosslinker, respectively, to improve weak mechanical properties of silicone rubber (SR). Structures of the crosslinkers were studied by gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR), and nuclear magnetic resonance (NMR). Crosslinking density test and scanning electron microscope (SEM) observation showed an increased interaction between silicone rubber and fumed silica by the use of MMSCA. Mechanical properties of the resulted composites using MMSCAs were increased to varying degrees compared with those possessing crosslinkers without ethoxy group. MMSCAs were effective for further property enhancements of composites. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43415.

INTRODUCTION

Since dimethylsiloxane rubber was obtained by peroxide curing in 1940s, silicone rubber (SR) has been applied in many fields because of many excellent properties such as biocompatibility,[1–4] high thermal stability,[5–8] weather resistance,[9] oxidation resistance,[10] good permeability,[11,12] and low surface energy,[13] etc.

Main chains of the silicone rubber exhibit weak intermolecular forces due to their special chain structures. Some related investigations[14,15] had been done to enhance rubber mechanical properties. Use of fumed silica and improving the crosslinking network are two main effective ways.

Silane coupling agent (SCA) is beneficial for improving interactions between inorganic fillers and polymeric matrix. Wang et al.[16] used the calcium sulfate whisker fibers treated by KH-560 as the reinforcement filler of silicone rubber and got higher mechanical properties compared with those untreated. Yi et al.[11] and Zhou et al.[12] modified silicalite-1 with vinyltrimethoxysilane and improved the affinity between silicalite-1 and polydimethylsiloxane. Performances of hybrid pervaporation membrane were improved. Liu et al.[17] found that combinational use of KH-550 and KH-560 can significantly improve the bonding strength of samples compared with that of single silane. The

reason was ascribed to the reactions between amide groups of KH-550 and epoxy groups of KH-560. By means of Fourier transform infrared spectroscopy (FTIR) and energy-filtering transmission electron microscopy (EFTEM), Dohi et al.[18] and Liu et al.[19] observed SCA weakens the interactions between the inorganic fillers. A coupling layer was formed between inorganic fillers and polymer matrix and enhanced the interface forces. Tai et al.[20] anchored macromolecular coupling agent on the surface of nano-SiO$_2$ and the results showed superior to small molecular coupling agent.

Many efforts were made to obtain better mechanical properties of SR by improving the crosslinking network. Use of concentration crosslinking is an effective method. Xu et al.[21] and Cao et al.[22] reported the crosslinkages formed in high vinyl content region distributed stress well and improved properties of SR. They also gave their cross-linked network model. Xu et al.[23] used polysiloxanes containing phenylethynyl groups as crosslinker and Zhao et al.[24] used vinyl-containing silicone resin as the crosslinker. Both methods improved mechanical properties. Zhao et al.[25] found that use of allyl-capped carbosilane dendrimers of different generations as crosslinker presented a good concentration crosslinking effect. Tensile strength was increased from 8.4 MPa to 10.1 MPa, and tear strength was increased from 27.5 kN m^{-1} to 32.0
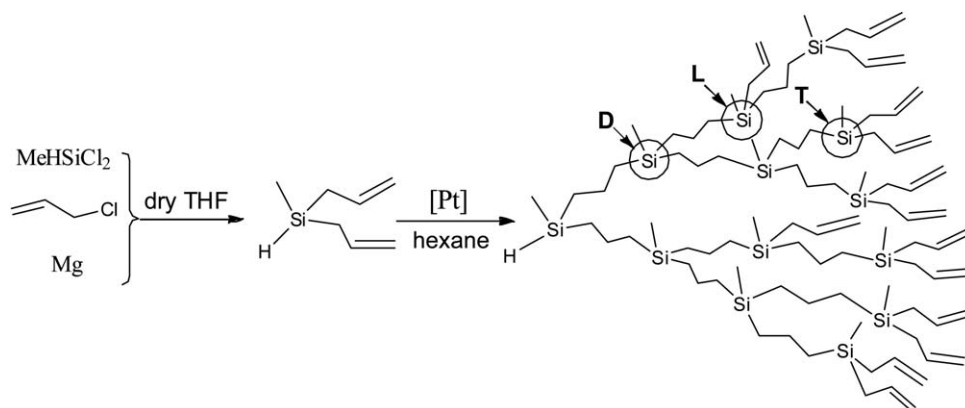
Scheme 1. Synthesis process of allyl-capped hyperbranched polycarbosilane.

Table I. Data of Titration Tests

	Blank sample	1	2	3
M_{HBP}/g	0	0.0233	0.0360	0.0392
V_{STSS}/mL	26.86	19.48	15.50	14.58
Mass fraction ω (vinyl)		21.66%	21.58%	21.42%
Average value		21.55%		

$kN\ m^{-1}$. Han et al.[26] prepared polymethoxysiloxane with dense pendant silicone-methoxy groups and found in-situ reinforcement improved comprehensive properties of SR composites. Chen et al.[27–31] synthesized divinylhexa[[(trimethoxysilyl)ethyl]-polyhedral oligomeric silsesquioxane (POSS) via hydrosilylation of vinyl-POSS and trimethoxysilane and used it as crosslinker. Combinational use of fumed silica as reinforcing filler, the resulted tensile strength of Room Temperature Vulcanized silicone rubber was increased by two times.

Allyl-capped hyperbranched polycarbosilane (HBP) are highly branched polymer with a large number of vinyl groups. Low-viscosity of hyperbranched polymer is caused by the arrangement of branches in different directions and thus little branch entanglement happens. Its special property might contribute to a good dispersion of fumed SiO_2 and it could replace vinyl silicone oil (VSO) as crosslinker of SR composites.

In this work, we prepared macromolecular silane coupling agents (MMSCAs) via hydrosilylation of triethoxysilane (TES)

with three different macromolecules, which involved two types of polysiloxane oils with different vinyl content and allyl-capped polycarbosilane with hyperbranched structure. Structures of VSOs, HBP, and MMSCAs were characterized by GPC, IR, and NMR. They were used as silicone rubber crosslinker respectively. Morphology, crosslinking density, mechanical properties, and thermal stabilities of corresponding SR composites were investigated by scanning electron microscope (SEM), equilibrium swelling method, Universal Testing Machine (UTM), and thermal gravity analysis, respectively. The functional mechanism of MMSCA on improving mechanical properties and thermal stabilities of SR composites were proposed.

EXPERIMENTAL

Materials

Poly(dimethyl/methylvinylsiloxanes) (PDMS, STARSIL[TM]GUM753) was supplied by Blue Star Chemical New Material Co., China, with the average molecular weight of about 630,000 g mol^{-1} and the vinyl content of 0.14 mol %. The fumed silica TS-530 was purchased from Cabot Co. Vinyl silicone oil (VM-26,) specified as VSO-1, was provided by Zhejiang Quzhou Jian Cheng Silicone Co., China with the vinyl content of 8.61 mol %. Another vinyl silicone oil (VSO-2) with the vinyl content of 18.03 mol % was prepared in our laboratory. Molecular weights were tested by gel permeation chromatography (GPC, Viscotek 270 max, Melvin Instrument Co., Britain). 2,5-Bis(tert-butylperoxy)-2,5-di-methylhexane (DBPMH) was purchased from Akzo Nobel Peroxide Co., Tianjin, China. Magnesium turning was obtained from Tianjin Kermel Chemical Reagent Co., China. Dichloromethylsilane (AR) was received from Aladdin reagent (Shanghai) Co., China. Triethoxysilane (AR), chloroplatinic
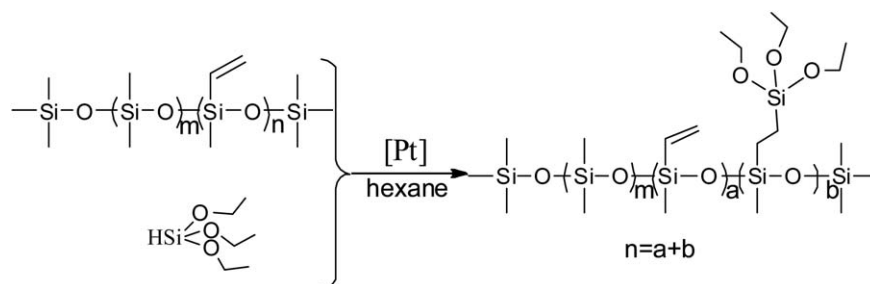
Scheme 2. Synthesis process of MMSCA-1 and MMSCA-2.
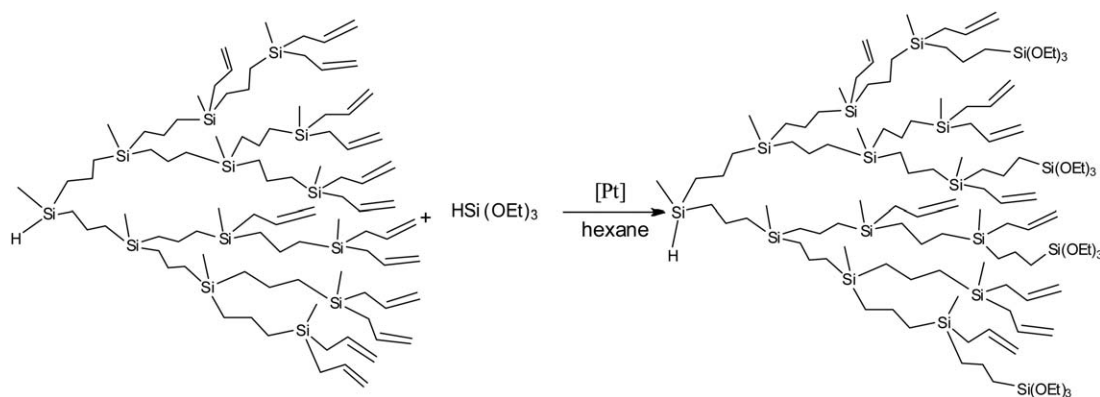
Scheme 3. Synthesis process of MMSCA-3.

acid (AR), tetrahydrofuran (AR), sodium thiosulfate (AR), carbon tetrachloride (AR), iodine bromide (AR), n-hexane (AR), and toluene (AR) were supplied by Sinopharm Chemical Reagent Co. Karstedt's catalyst was prepared by refluxing of chloroplatinic acid and 1,1,3,3-tetramethyl-1,3-divinyldisiloxane at 138–142 °C for 90 min. Tetrahydrofuran and hexane were distilled over sodium/benzophenone. Carbon tetrachloride solution of iodine bromide was prepared in our laboratory. Chemicals were freshly distilled before use. Reactions were carried on with N_2 protection except hydrosilylation, which was carried in sealed system.

Synthesis of Allyl-Capped Hyperbranched Polycarbosilane

Magnesium turning (26.75 g) and dried tetrahydrofuran (100 mL) were added to a 1000 mL three necked round bottom flask with the protection of nitrogen. Mixed solution of allyl chloride (90 mL), dichloromethylsilane (52 mL), and tetrahydrofuran (350 mL) was dropwise added in the flask for 10 h with stirring. After the addition, the mixture was stirred for extra 10 h. The reaction was ended by addition of 300 mL deionized water. The organic layer was obtained by separation after standing for 6 h. A colorless liquid was obtained after the solvent was removed by evaporation at 80 °C. Then the product (monomer) was dried over anhydrous $MgSO_4$ (6 g) for 6 h and separated. **Monomer**: ^{1}H NMR (400 MHz, CDCl$_3$, δ): 0.10–0.20 (d, $J = 3.64$ Hz, 3H, Si—CH$_3$), 1.66–1.70 (m, $J = 13.88$ Hz, 4H, Si—CH$_2$), 3.87–3.92 (oct, $J = 16.56$ Hz, 1H, Si—H), 4.91–4.95 (2H, CH=CH$_{2,trans}$), 4.95–4.99 (2H, CH=CH$_{2,cis}$), 5.79–5.90 (2H, CH=CH$_2$). ^{13}C NMR (400 MHz, CDCl$_3$, δ): −7.43 (Si–CH$_3$), 19.78 (Si—CH$_2$—;), 113.6 (—CH=CH$_2$), 134.0 (CH=CH$_2$). ^{29}Si NMR (400 MHz, CDCl$_3$, δ): $\delta = -12.70$.

The liquid product (5 mL), hexane (25 mL) and Karstedt's catalyst (2 drops) were added to a 250 mL round bottom flask with the protection of nitrogen. The system was sealed and refluxed

for 8 h at 75∼80 °C with stirring. The solvent was evaporated and allyl-capped HBP, a viscous liquid was obtained. The reaction was shown in Scheme 1. **Allyl-capped HBP**: ^{1}H NMR (300 MHz, CDCl$_3$, δ): −0.07–0.14 (Si–CH$_3$), 0.52–0.65 (S—CH$_2$CH$_2$CH$_2$—Si), 0.94–1.03 [Si—CH(CH$_3$)CH$_2$—Si], 1.25–1.41 (Si—CH$_2$CH$_2$CH$_2$—Si), 1.50–1.63 (CH$_2$—CH=CH$_2$), 1.80–1.83 [Si—CH(CH$_3$)CH$_2$—Si], 4.80–4.89 (CH=CH$_2$), 5.70–5.99 (CH=CH$_2$). ^{13}C NMR (300 MHz, CDCl$_3$, δ): −5.8 to −5.0 (Si—CH$_3$), 17.8–18.9 (Si—CH$_2$—CH$_2$—CH$_2$—Si), 21.4–22.8 (CH$_2$—CH=CH$_2$), 112.6–113.5 (CH=CH$_2$), 133.9–135.3 (CH=CH$_2$). ^{29}Si NMR (300 MHz, CDCl$_3$, δ): 0.20 (terminal unit), 0.66 (linear unit), 0.95 (dendritic unit).

Titration Tests

Certain amount of allyl-capped HBP was added to a conical flask and 30 mL carbon tetrachloride was added to dissolve it. Then carbon tetrachloride solution of iodine bromide (10 mL) and potassium iodide solution (8 mL) were successively added. After every addition, sufficient shock was necessary to make the reaction completed. Then $Na_2S_2O_3$ standard solution (0.05066 mol L^{-1}) was dropwise added into the above mixture with constant shock. When the mixture was nearly colorless, starch indicator (3 mL, 0.005 g mL^{-1}) was put in the conical flask and the dropwise addition was going on until the mixture was colorless. The titration test was performed for three times and the blank test was performed in the same condition. Test data was shown in Table I. Mass fraction of vinyl groups in HBP was calculated by the following equation:

$$\omega = 0.05066 \times 27 \times (V_0 - V_n)/(M_{HBP} \times 2000) \times 100\% \quad (1)$$

where V_0 is the consumption the volume of $Na_2S_2O_3$ standard solution for blank sample, and V_n is the consumption volume of $Na_2S_2O_3$ standard solution for three groups of titration tests of HBP.

Table II. Synthetic Source of Macromolecular Silane Coupling Agents

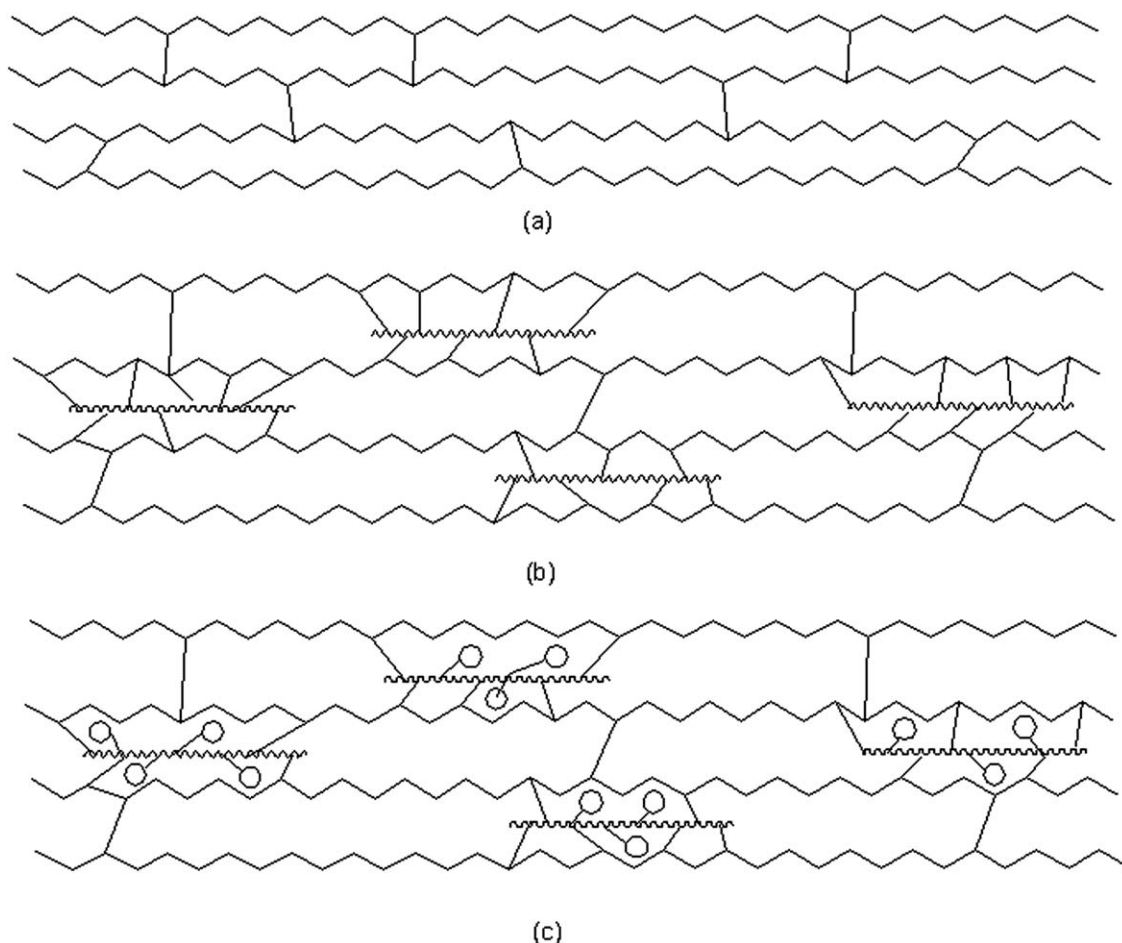| Serial number	VSO-1/g	VSO-2/g	HBP/g	TES/g	Hexane/mL	Karstedt's catalyst/drop
MMSCA-1	9.62	–	–	1.25	50	4
MMSCA-2	–	10.00	–	2.00	50	4
MMSCA-3	–	–	4.01	2.66	25	2

Figure 1. Comparison of crosslinking network of SR using different crosslinker. (a) Crosslinking network of SR only crosslinked by vinyl groups of PDMS (long broken lines), (b) crosslinking network of SR using macromolecules (short wavy lines) as crosslinker, and (c) crosslinking network of SR using MMSCA (short wavy lines) as crosslinker anchoring some fumed SiO2 (hollow rounds).

GPC Tests

A standard sample of polystyrene was used as reference for GPC tests. Firstly, a toluene solution of VSOs was prepared 6 h in advance to make the dissolution completed. Then, the solution (100 mL) was injected into testing system with a toluene elution velocity of 1.0 mL min^{-1} at 25 °C. Results were obtained.

Synthesis of Macromolecular Silane Coupling Agents

We prepared three MMSCAs through the same preparation. A mixture of certain amount of macromolecule, hexane, TES, and Karstedt's catalyst was stirred and kept refluxing at 70 °C for 8 h with N_2 protection. The solvent was distilled and the resulting mixture was kept air-free. The reaction is shown in Schemes 2 and 3. Data of reactants is listed in Table II. Changes of the chemical structures before and after the reaction were monitored by Fourier transform infrared spectroscopy (FTIR) and ^1H NMR, respectively, as shown in Figures 1 and 2. The red numbers represent integrals of hydrogen atoms.

VSO: ^1H NMR (300 MHz, $CDCl_3$, δ): 0.04–0.15 (Si—CH_3), 5.75–6.07 (CH═CH_2) **MMSCA-1** and **MMSCA-2**: ^1H NMR (300 MHz, $CDCl_3$, δ): 0.04–0.20 (Si—CH_3), 0.49–0.56 (Si—CH_2—), 1.20–1.27 (O—CH_2—CH_3), 3.73–3.90 (O—CH_2—), 5.74–6.07 (CH═CH_2) **MMSCA-3**: ^1H NMR (300 MHz, $CDCl_3$,

δ): −0.07–0.14 (Si—CH_3), 0.59–0.69 (Si—$CH_2CH_2CH_2$—Si), 0.90–1.03 [Si—$CH(CH_3)CH_2$—Si], 1.24–1.41 (Si—CH_2CH_2 CH_2—Si, O—CH_2—CH_3), 1.45–1.60 (CH_2—CH═CH_2), 1.80–1.85 [Si—$CH(CH_3)CH_2$—Si], 3.73–3.90 (O—CH_2—), 4.83–4.93 (CH═CH_2), 5.74–5.88 (CH═CH_2).

Composites Preparation

Formulations of the silicone rubber composites are shown in Table III. The composites were prepared in an open mixing mill with double rollers, XK-160 (Qingdao Guangyue Rubber Machine Makes Co., China) at room temperature. Fumed SiO_2 was continuously added to silicone gums, then crosslinker was added, and the gums were mixed for an extra time. The mixed gums covered by a paper were kept in air for 24 h and were put in an air-circulating oven at 175 °C for 2 h. After cooling to room temperature, vulcanizing agent DBPMH was added and the gums were mixed by rollers again for 10 min. Then, the mixed gums were vulcanized in a mold at 170 °C, 10 MPa for 25 min by a plate vulcanizer machine, XLB400 × 400×2 (Qingdao Guangyue Rubber Machine Makes Co., China). Post-vulcanization was carried out at 180 °C for 2 h in an air-circulating oven. The data in Table III is mass fraction of materials.
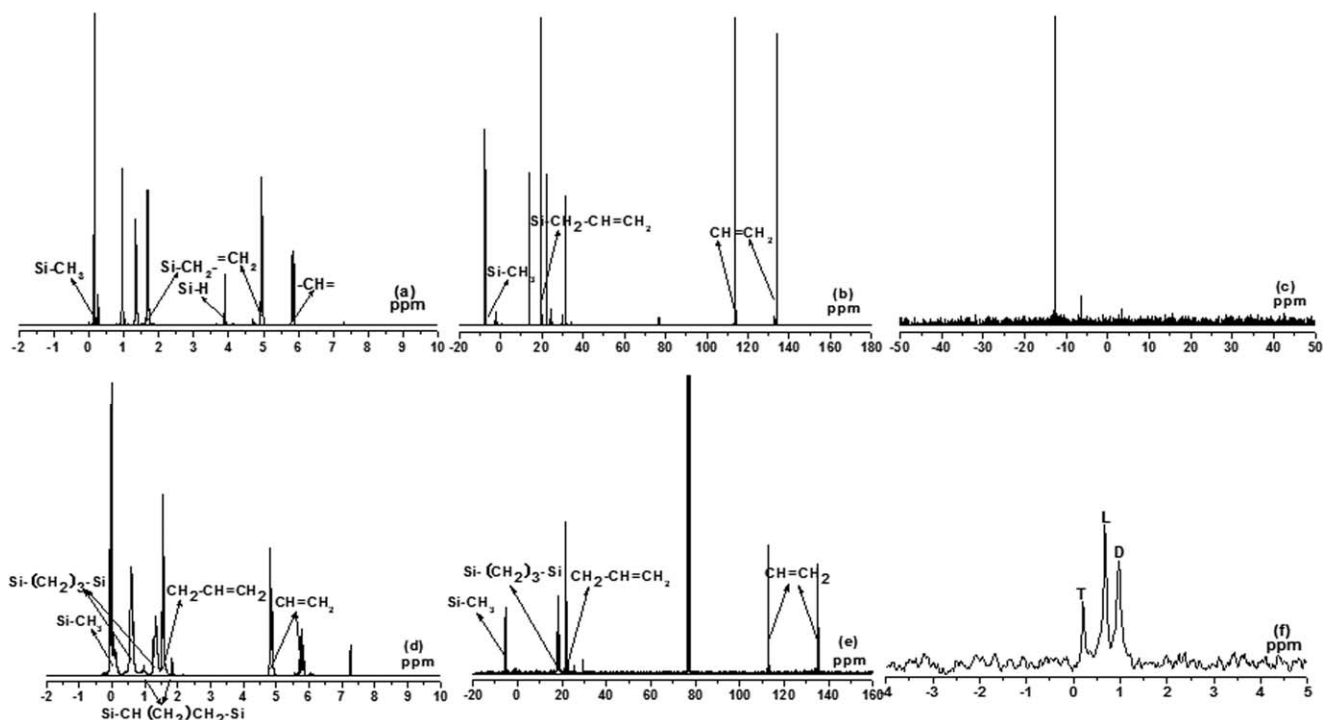
Figure 2. (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) ^{29}Si NMR of diallylmethylsilane; and (d) ^{1}H NMR, (e) ^{13}C NMR, and (f) ^{29}Si NMR of allyl-capped HBP.

Crosslinking Density Testing

Vr, the volume change rate of rubber before and after swelling, is an index of the crosslinking density. It was measured by the equilibrium swelling method.[21,32] Firstly, each sample (0.2~0.3 g) was added in a 25 mL bottle, respectively, and toluene (10 mL) was added. The swelling process was performed at room temperature. After swollen for 72 h, they were removed from the solvent and weighted immediately when the sample surface was blotted up. The swollen process was completed until the mass difference of every 6 h was less than 0.01 g. Then the samples were dried in vacuum at 60 °C for 6 h. V_r is determined by the following eq. (2):

$$V_r = [m_0 \phi \rho_r^{-1}] / [m_0 \rho_r^{-1} + m_1 \rho_s^{-1}] \times 100\% \qquad (2)$$

where m_0 is the sample mass before swelling, m_1 is the weight of the absorbed solvent, φ is the mass fraction of rubber in the

Table III. Formulation of the Silicone Rubber Composites

Sample	Silicone gums	TS-530	Crosslinker	DBPMH
S.1	100	60	3.0 (VSO-1)	1.5
S.2	100	60	3.0 (MMSCA-1)	1.5
S.3	100	60	3.0 (VSO-2)	1.5
S.4	100	60	3.0 (MMSCA-2)	1.5
S.5	100	60	0.8 (HBP)	1.5
S.6	100	60	0.8 (MMSCA-3)	1.5
S.7	100	60	1.6 (HBP)	1.5
S.8	100	60	1.6 (MMSCA-3)	1.5
S.9	100	60	3.0 (HBP)	1.5
S.10	100	60	3.0 (MMSCA-3)	1.5

vulcanizate, and ρ_r and ρ_s are the densities of the rubber and solvent, respectively. The densities of SR composites were tested by specific gravity method.

Mechanical Tests

The mechanical property testing was carried out according to GB/T 528-2009 by an electronic Universal Testing Machine, UTM4203 (Shenzhen Suns Technology Stock Co., China). The tensile strength, elongation at break, and tear strength were measured at a crosshead speed of 500 mm min^{-1}. Dumb bell-shaped specimens (initial length was 20 mm and width 4 mm) were punched out from vulcanized sheet. Four specimens were measured for each formulation by the same stretch rate.

Morphology Characterization

Morphological observation of the silicone rubber was done with thermal field emission scanning electron microscope (SEM, SU-70, HITACHI Instruments). Samples were fractured in liquid nitrogen, and were coated with a thin gold layer by a special coating machine.

Thermal Properties

Thermal gravimetric analysis (TGA) was performed by Labsys Evolution STA (SETARAM instrument, France). About 10 mg sample was heated in an alumina crucible from room temperature to 800 °C under argon. The heating rate was 10 °C min^{-1}.

RESULTS AND DISCUSSION

Synergistic Effect of MMSCA

Crosslinking density is necessary for stress distribution and a proper value is favored to obtaining optimized properties. To obtain a best value of crosslinking density, a suitable dosage of vinyl silicone oil, which was added in silicone rubber, is
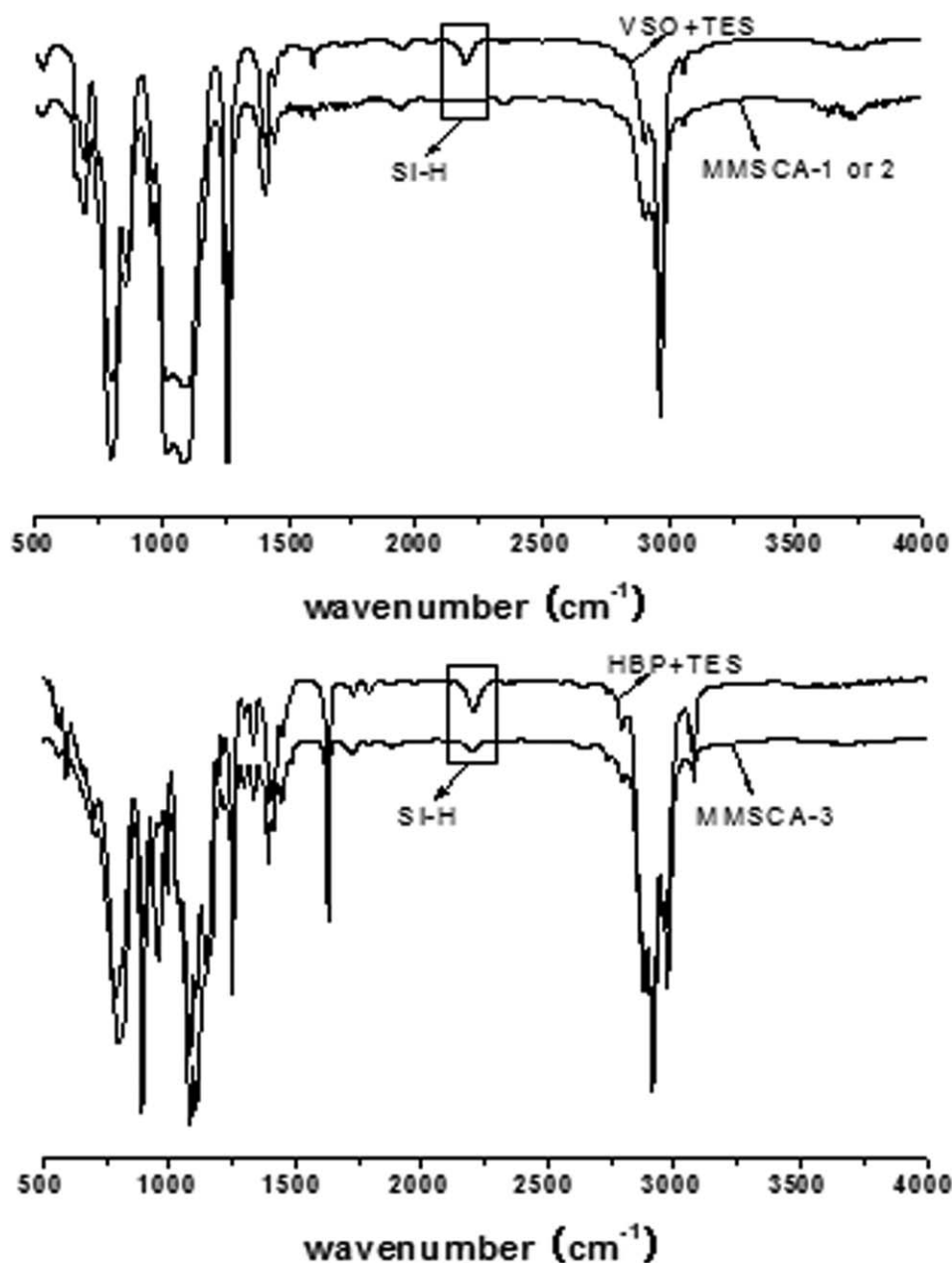
Figure 3. FTIR spectra of reactants and hydrosilylated products.

extremely important. However, the strength is limited just through the addition of vinyl silicone oil. MMSCAs are helpful to further improvement for properties of SR. They were prepared by hydrosilylation and both contained vinyl and ethoxy groups. Hydroxyl groups hydrolyzed by ethoxy groups could anchor some fumed SiO_2 fillers by condensation reaction and thus strengthens the interactions between inorganic part and polymeric matrix by chemical bonding. Therefore, a hybrid crosslinking structure was formed and a better comprehensive mechanical property could be expected. We call this synergistic effect of MMSCA.

The functional mechanism of different crosslinker in PDMS molecules is shown in Figure 3. There are more crosslinkages generated by concentration crosslinking of the macromolecules

in Figure 3(b) than (a). Those crosslinkages can disperse stress well.[20,21] The short wavy lines represent MMSCA in Figure 3(c). Introduction of ethoxy groups on VSOs and HBP makes the crosslinkages anchoring some SiO_2. A hybrid crosslinking network is formed at the edges of the crosslinkages. Moreover, partial vinyl groups are consumed and it prevents the silicone rubber from hardening.

Table IV. Structural Parameters of the Macromolecules

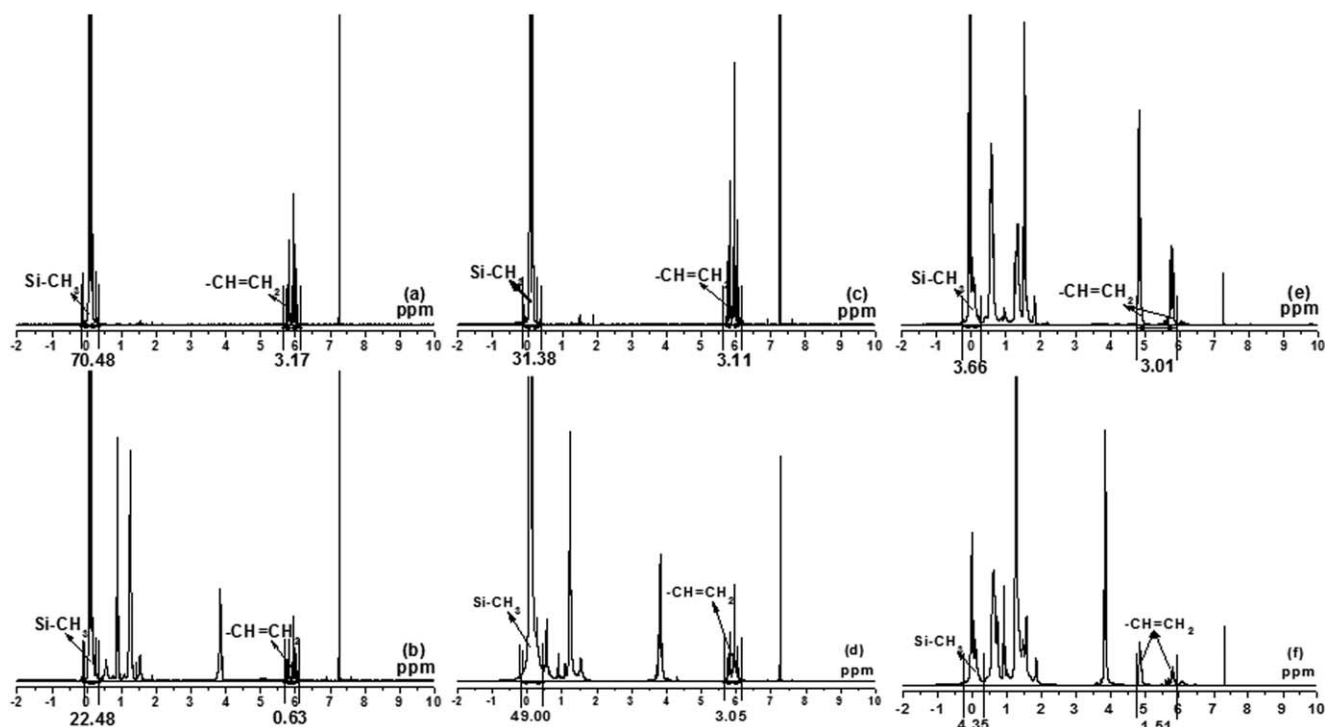|	Mω (g/mol)	Mω/Mn	dn/dc	Log K	α
VSO-1	80,026	1.717	0.1123	−4.321	0.746
VSO-2	33,909	2.534	0.1828	−3.983	0.765

Figure 4. ^{1}H NMR spectra of (a) VSO-1, (b) MMSCA-1, (c) VSO-2, (d) MMSCA-2, (e) HBP, and (f) MMSCA-3.

Structural Analysis of the Macromolecules and MMSCAs

Structures of the macromolecules and the monomer were characterized by NMR and GPC, as can be seen from Figure 1 and Table IV. The results by GPC reveal that vinyl silicone oils present molecular weight of 80,026 and 33,909. According to the NMR analysis, allyl-capped HBP shows the similar structures with what Zhang et al.[33] prepared. The 2197 cm^{-1} (Si—H stretching vibration mode) absorption peak weakens as the hydrosilylation reaction takes place in Figure 2. According to ^{1}H NMR analysis of VSOs, their vinyl contents (mole fraction) are 8.61% and 18.03%, respectively, and vinyl mass fractions are 3.10% and 6.39%. In the preparation of MMSCA, content of hydrogen atoms in Si—CH$_3$ is constant, while that of hydrogen atoms in —CH=CH$_2$ is gradually reduced with the reaction progress. P, defined as consumption ratio of vinyl groups or bounding ratio of TES, is calculated by eq. (3):

$$P=100\%-S_2'\times[(S_1-S_2)/2+S_2]/S_2\times[(S_1'-S_2')/2+S_2'] \quad (3)$$

where S_1, S_2, S_1', and S_2' are integral area of hydrogen atoms in Si—CH$_3$ and —CH=CH$_2$ before and after the reaction, respectively. Results calculated through eq. (3) show that the consumption ratio of vinyl groups in the preparation of MMSCA-1 is 36.59%. Similarly, the consumption ratio of vinyl groups in the preparation of MMSCA-2 is 35.00%. Content of vinyl groups in HBP also decreases rationally. The integral area of hydrogen atoms in Si—CH$_2$— ($\delta = 0.5\sim0.8$) for all the MMSCAs enlarges when compared with the macromolecules and there are ethoxy groups ($\delta = 3.7\sim3.9$) in Figure 4. It indicates that the reaction between —CH=CH$_2$ and Si—H took place. The above results of IR and ^{1}H NMR agree with each other. These reveal that MMSCAs are successfully prepared and

they contain plenty of vinyl groups and ethoxy groups at the same time.

SEM Morphology of SR Composites

Figure 5 are the images of cross-section morphologies of samples from S.1 to S.10. Images show that fumed SiO$_2$ can be well dispersed in polymeric matrix. Comparing images from (a) to (d) in Figure 5, the samples using MMSCA present more tiny ripples regions in rectangle curves. It could be ascribed that synergistic effect of MMSCA enhances the interactions of components. Further observations are performed with greater magnification shown in images from (e) to (n) Figure 5. Fumed SiO$_2$ in samples using crosslinkers with hyperbranched structures disperses better, which is linked closely to low viscosity property of HBP. It is consistent with the proposed assumption mentioned above. Moreover, samples using MMSCA show more micropores for S.2 with S.4 and more pyknotic micropores for S.6, S.8, and S.10. It seems that the interaction in the interior of those samples is more powerful.

Crosslinking Density of SR Composites

It is necessary to crosslink the rubber chains into the network to obtain the desired physical properties. However, excessive crosslinking causes the flexibility decreases and the hardness increases. Appropriate crosslinking density is required to strengthen rubber's properties. Figure 6 shows the results of crosslinking densities of the silicone rubber samples (from S.1 to S.10) and they are calculated according to eq. (2). The blank columns represent S.E.-frees (samples whose crosslinkers are free of ethoxy group), and gray columns represent S.E.s (samples whose crosslinkers contain ethoxy group). As can be seen from Figure 6, crosslinking densities of the S.E.-frees increase
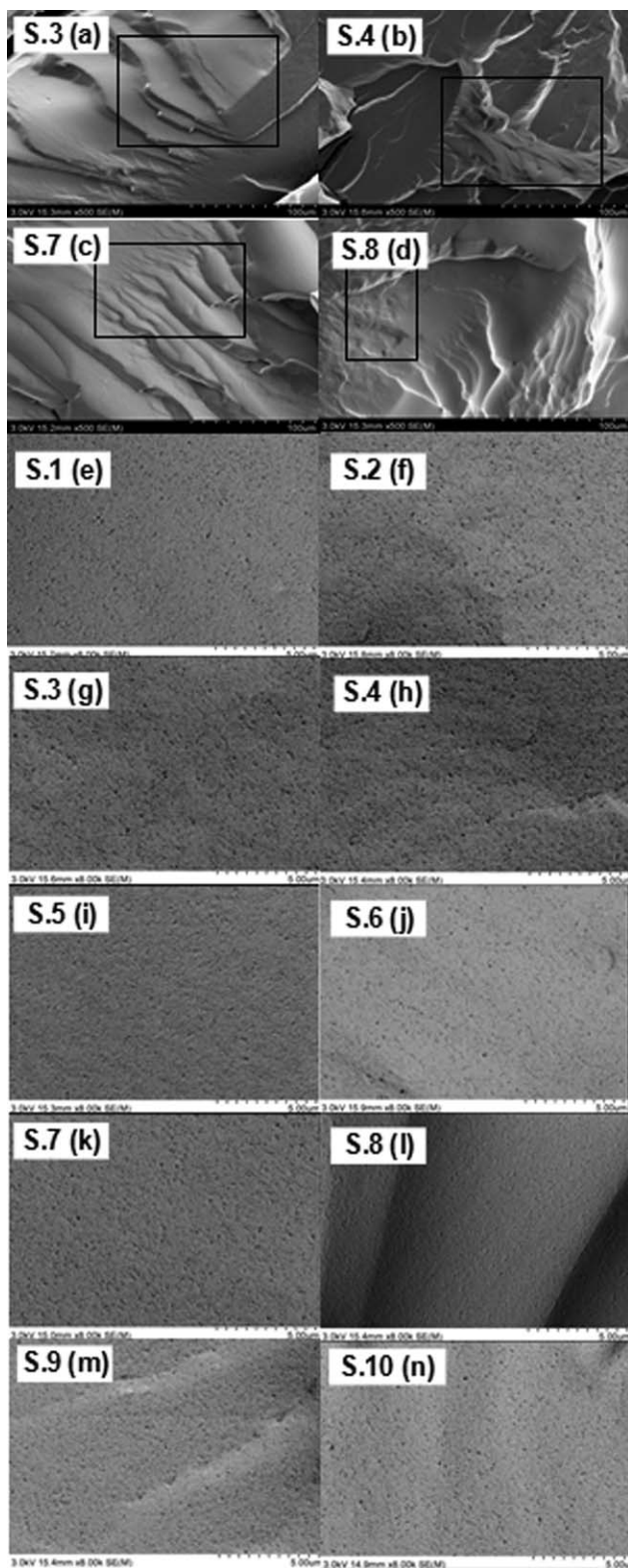
Figure 5. Cross-section morphologies of samples from S.1 to S.10.

caused by an excess of vinyl groups enhances interaction between PDMS molecules. However, there is different variation trend for S.E.s. When vinyl content is relatively low, the crosslinking action generated by the vinyl groups change slightly, and the introduction of ethoxy groups more effectively enhanced the interaction between components for S.2, S.4, and S.6. This made them possess higher crosslinking density than S.1, S.3, S.5, respectively. With the vinyl content increasing, the crosslinking density of S.E.s (S.8 and S.10) is lower than S.E.-frees (S.7 and S.9). The reason may be that when the vinyl content is overmuch, the interaction between macromolecule chains increases markedly and crosslinking densities are improved correspondingly. At this moment, the introduction of ethoxy groups reduces content of vinyl groups in HBP, sequentially, crosslinking densities decrease.

Mechanical Properties of SR Composites

The mechanical properties for composites have a close relationship with crosslinking network of rubber. The mechanical properties of all the samples from S.1 to S.10 (from left to right) are shown in Figure 7 and their stress–strain curves are presented in Figure 8. As can be seen from Figure 7, S.E.s show higher tensile strength and tear strength than the S.E.-frees. For tensile strength, the S.E.s increase by 8.13%, 4.46%, 8.42%, 11.86%, and 8.07% when compared with the S.E.-frees, respectively, and for tear strength, the S.E.s increase by 13.02%, 17.90%, 9.28%, 5.52%, and −0.02% when compared with the S.E.-frees. In addition, with vinyl and ethoxy content of MMSCA gradually increasing from S.1 to S.8, tensile strength and tear strength rise to the maximum value of 11.22 MPa and 21.80 kN m^{-1}, respectively. Those enhancements could be owed to crosslinking networks of MMSCAs as shown in Figure 3(c). They strengthen the interactions among the components and yield better mechanical properties. However, excessive crosslinking leads to harden of SR composites and decreases their mechanical properties. With the dosage of crosslinker from 1.6 phr to 3 phr, the tensile strength and tear strength of the samples for S.9 and S.10 decrease relatively. The stress–strain curves in Figure 8 show that the S.E.s show higher tensile modulus than the S.E.-frees from S.1 to S.6 owing to synergistic effect of MMSCA. However, with vinyl content in crosslinker increasing, the trend is opposite from S.7 to S.10. It could be interpreted as obvious enhancement of interaction between PDMS molecules caused by excessive crosslinking of vinyl groups. Introduction of ethoxy groups reduces vinyl content and prevents samples hardening. It thus improves toughness of S.8 and S.10, respectively, compared with S.7 and S.9. MMSCA is helpful to improve mechanical properties of SR composites.

Thermal Gravimetric Analysis

When silicone rubber was placed at a continuous temperature-rise period, there are two degradation regions (degradation of pendant groups and degradation of main chains). Thermal stability of some samples is illustrated by TGA and dTG curves in Figure 9. All the samples show similar trend. It could be interpreted as that, all samples contained same composition. The obvious change is not obtained. The degradation trend for S.2
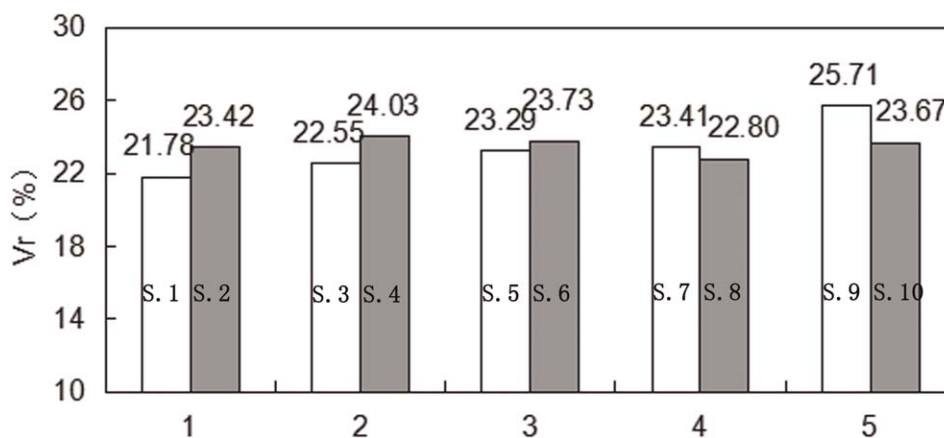
successively. The reason could be ascribed that vinyl content (21.55%) of allyl-capped HBP is much greater than VSOs (3.10% and 6.39%), and excessive crosslinking in SR composites

Figure 6. Crosslinking densities of samples from S.1 to S.10.

moves to a little higher temperature than S.1. It could be attributed to ethoxy groups of MMSCAs, which anchored some fumed SiO_2 and hindered the rearrangement degradation of main chains better. When the content of vinyl groups increases for S.5 and S.6, however, there is no difference for their trends. The reason could be interpreted that the degree of obstruction for degradation has reached a higher level, and there is no change for the samples. It thus could be considered that introduction of ethoxy groups is not beneficial for further improvement of thermal stability.

CONCLUSIONS

In this article, MMSCAs were successfully prepared via hydrosilylation. VSOs, HBP, and MMSCAs were used as crosslinker of silicone rubber respectively. Low-viscosity of HBP is helpful for uniformity of components. The S.E.s show better mechanical properties compared with the S.E.-frees when the content of vinyl groups in crosslinker is relatively low. The maximum of growth ratio for tensile strength and tear strength reaches to 11.86% and 17.60%, respectively. With vinyl content in crosslinkers increasing, introduction of ethoxy groups can strengthen
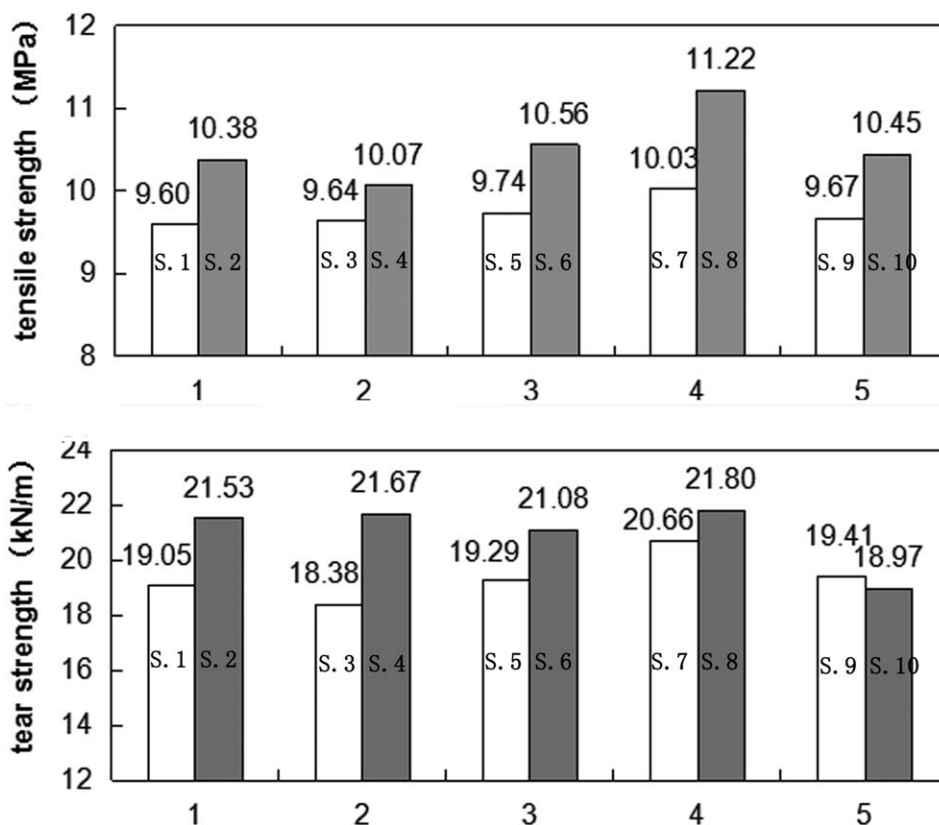

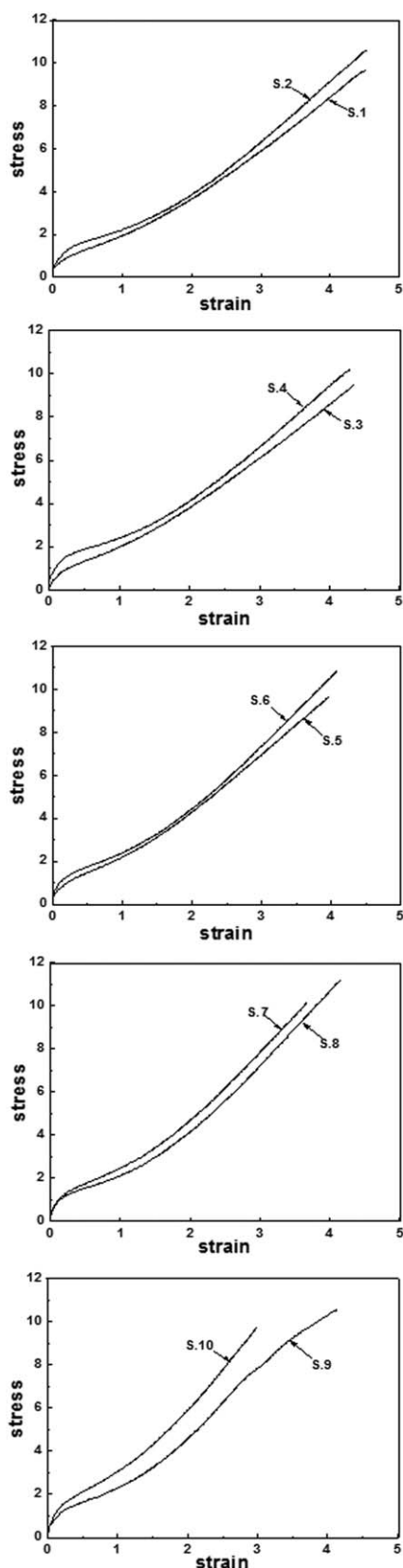**Figure 7.** Tensile strength and tear strength of samples from S.1 to S.10.

Figure 8. Stress–strain curve of samples from S.1 to S.10.
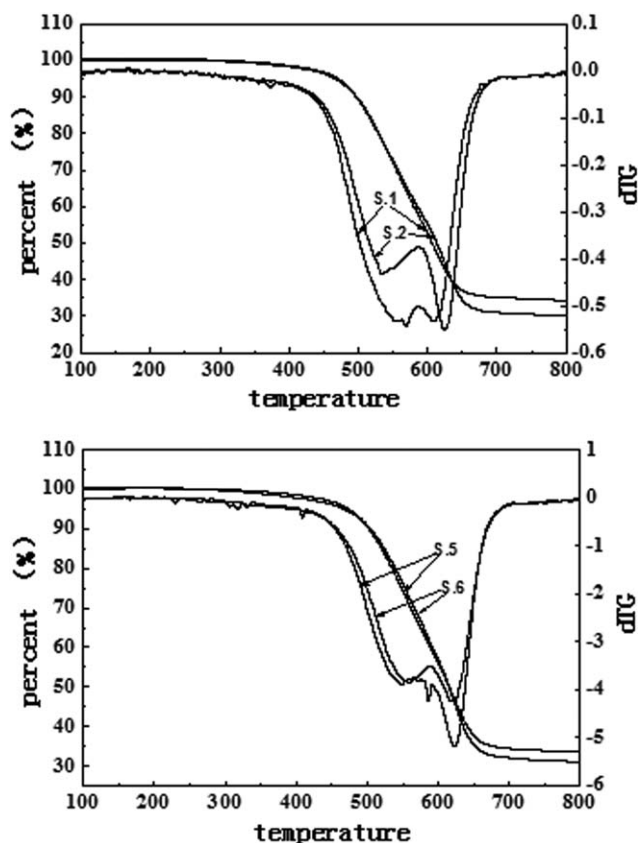

Figure 9. TGA and dTG curve of samples.

toughness of silicone rubber by reacting off partial vinyl groups of the macromolecules. It turns out that synergistic effect of MMSCAs improves rather effectively mechanical properties of silicone rubber. They should be widely applied in rubber field as crosslinker. However, there is no contribution for thermal stability and action of MMSCAs is not controlled quantitatively. Hydrolysis condition of ethoxy groups in the preparation of composites needs further study to ensure action of MMSCAs to reach an optimum efficiency.

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