Synthesis and Characterization of Novel Fluorosilicone Rubber Using Imide Modified Vinyl-Containing Fluorosilicone Resin as Cross-Linker

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ABSTRACT: A novel imide modified vinyl-containing fluorosilicone resin (MP-VFS) was firstly prepared from maleopimaric acid (MPA), and characterized by ^{1}H NMR and ^{13}C NMR. Containing MPA based imide heterocycle (MPABI), MP-VFS was further used as a novel cross-linker to prepare MPA modified fluorosilicone rubber (MP-FSR). Morphology, mechanical and oil-resistance properties, thermal properties, and low temperature resistance of MP-FSR had been studied. Microphase separation was observed in MP-FSR. Although the tensile strength of fluorosilicone rubber was not significantly enhanced, the tearing strength, breaking elongation, rebound resilience and hardness were effectively improved. When the MP-VFS content was 2.0 wt %, the tearing strength of MP-FSR was increased by 23.5%, breaking elongation by 18.6% and rebound resilience by 9.7%. The thermal stability was enhanced due to the incorporation of MPABI. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, *53*, 1769–1776

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INTRODUCTION Fluorosilicone rubber, due to the combined structure of fluorocarbon and polysiloxane, has many unique properties, such as fuel oil resistance, heat resistance, low temperature flexibility, chemical inertness, and low surface energy.[1–10] Poly[methyl(trifluoropropyl)siloxane] rubber, is the first and still the most common fluorosilicone rubber.[10] It offers the best low temperature properties of any oil resistant rubber, and is primarily used as sealants and gaskets in the aviation and automotive industries.[1,5] However, like all silicone rubbers, fluorosilcone rubber also has the drawbacks of relatively low mechanical strength, which limits its practical application.[11,12] To overcome this problem, considerable efforts have been done, mainly including adding reinforcement filler,[12] blending with other high-strength polymer,[13] using different crosslinking agent[14] or crosslinking system.[11] Given the effective improvement of mechanical strength, the choice of a novel crosslinking agent[14–17] or crosslinking system[11] has attracted more and more attentions in recent years. Effects of vinyl-containing silicone resin on the mechanical strength of silicone rubber has been studied in detail.[11,17] However, these researches are all based on the common vinyl-containing silicone resin.

Polyimide has outstanding comprehensive properties, such as high mechanical strength, excellent thermo-oxidative sta-

bility, and solvent resistance.[18–22] And all these properties should be more due to the strong rigidity and polarity of imide heterocycle. Theoretically, grafting imide heterocycle onto flexible fluorosilicone chain, would be a promising approach to increase the mechanical strength.[23] Considerable efforts have been made for the research of poly(imide-siloxane) copolymer, and more excellent mechanical properties and thermal stability have been obtained.[19–22] However, all these modifications occur at the backbone of polysiloxane and is very difficult to be maneuvered. No efforts have been found to grafting the imide heterocycle onto the side chain of polysiloxane, which should be a very convenient and promising method, concerning that the synthesis of polysiloxane backbone was based on the most common synthetic route (anionic or cationic ring-opening polymerization of cyclosiloxane).[22]

Maleopimaric acid (MPA) is the Diels-Alder adduct of rosin acids and maleic anhydride.[24] Since the carboxylic anhydride group (O=C—O—C=O) in MPA can easily react with amino group (-NH$_2$), it has been used to prepare imide compound in recent years.[25] Besides, as one type of rosin derivative, MPA contains large phenanthrene ring structure, and is similar to cycloaliphatic or aromatic compound in molecular

rigidity.[26,27] Therefore, it could be a good alternative to current petroleum-based rigid monomers, and has been demonstrated to be beneficial for improving the mechanical properties of polymers.[24,26,27] However, there have been no report on the preparation and characterization of imide modified fluorosilcone (MP-FSR) with MPA as the imidization agent.

In this article, a novel and imide modified vinyl-containing fluorosilicone resin (MP-VFS) was synthesized from MPA, and therefore MPA based imide heterocycle (MPABI) was grafted onto the side chain of vinyl-containing fluorosilicone resin. And then, with MP-VFS as a polar crosslinking agent, a series of MPA modified fluorosilicone rubbers (MP-FSR) were obtained. The influence of MP-VFS content (or MPABI content) on the mechanical properties, low temperature performance and thermal stability were studied in detail.

EXPERIMENTAL

Materials

D_3F (1,3,5-*tris*((3,3,3-trifluoropropyl)methyl)cyclotrisiloxane, purity $\geq$99.5%) was supplied by Shenzhen Guanheng New Materials Technology Co., Ltd. KOH (potassium hydroxide, purity $\geq$95%), MM (hexamethyldisiloxane, purity $\geq$99%), D_4Vi (1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane, purity $\geq$97%) and DBPH (2,5-*bis*(tert-butylperoxy)$-$2,5-dimethylhexane) were purchased from J&K Scientific Ltd. MPA was obtained according to literature.[24] HAPMS was obtained from the hydrolyzation of 3-aminopropyl(diethoxy)-methylsilane and then dehydrated under vacuum at 100 °C for 8 h. Fluorosilicone oil (a silanol end-stoped poly(methyltrifluoropropylsiloxane) with a viscosity of 104 mPa S) was obtained according to literature.[10] Fluorosilicone gum (poly(-methyltrifluoropropylsiloxane-*co*-methylvinylsiloxane), the weight percent of vinyl group is 0.16%, and the viscosity-average molecular weight is 1.1×10^6) was obtained according to literature.[28] Fumed silica HDK®N20 was purchased from Wacker.

Physicochemical Characterization

^{1}H NMR and ^{13}C NMR analyses were conducted with a Bruker DRX-500 nuclear magnetic resonance spectrometer with tetramethylsilane as the internal standard. Mechanical properties were measured in accordance with D2240, D412, D624, and D2632. Specific gravity was measured according to ASTM D792. Differential scanning calorimetry (DSC) measurement was performed on a Perkin-Elmer Diamond DSC instrument at a heating rate of 10 °C/min. The thermogravimetric analysis (TGA) was performed on a TG209F1 thermogravimetric analyser at a heating rate of 10 °C/min in a nitrogen flow (2 mL/min). The morphology was also investigated by scanning electron microscope (SEM; JSM-7600F, JEOL) on the new cut surface of FSR, which was sputter coated with platinum.

Average crosslink density (γ_e) can be calculated from the tensile strength (σ), breaking elongation (α), and the density of rubber (ρ), according to the following equation:[16]

$$\gamma_e = \frac{\sigma}{\rho RT(\alpha - \alpha^{-2})} \quad (1)$$

where R is 8.31 J/(mol·K) and T is room temperature.

Oil-resistance was measured by the percent change of mechanical properties before and after immersed in ASTM reference fuel C at 25 °C for 72 h according to ASTM D471. The mechanical strength (N), including tensile strength, breaking elongation, tearing strength, and hardness were investigated, and their percent changes ($\Delta N\%$) were calculated according to the following equation:

$$\Delta N\% = \frac{N_1 - N_2}{N_1} \times 100\% \quad (2)$$

where N_1 is the value of mechanical strength before immersion; N_2 is the value of mechanical strength after immersion.

In order to eliminate the influence of vinyl-containing fluorosilicone resin, common vinyl-containing fluorosilicone resin (C-VFS) and the corresponding fluorosilicone rubber (C-FSR) were also prepared and characterized. Micromorphology of MP-FSR was studied by scanning electron microscope (SEM).

Synthesis of MP-VFS and C-VFS

Imide modified vinyl-containing fluorosilicone resin (MP-VFS) was synthesized by the following steps: firstly, 7.2 g of D_3F, 9.0 g of MM, 20.2 g of D_4Vi, 15 g of HAPMS, and 0.1 wt % of KOH were mixed and dehydrated, and then heated to 100 °C; secondly, after 4 h reaction, 50 g of MPA was added into the flask and the mixture was slowly heated to 150 °C in about 4 h; finally, the system was pumped into vacuum to remove the volatile at about 180 °C. The corresponding preparation scheme of MP-FSR was shown Scheme 1, the NMR results of MP-VFS are listed as following:

^{1}H NMR (300 MHz, CDCl$_3$, δ): 0–0.3 (Si-CH$_3$), 5.4 (CH=C in MPABI), 5.6–6.2 (Si—CH=CH$_2$), 3.0 (CH$_2$—N), 3.1–3.4 (CHC=O in MPABI), 0.3–2.8 (Si=CH$_2$CH$_2$, =CH$_2$CF$_3$ and the other protons of MPABI).[4,25]

^{13}C NMR (75 MHz, CDCl$_3$, δ): 184 (COOH), 176–179 (O=C-N-C=O), 145 (CH=$\underline{C}$ in MPABI), 136 (Si—CH=$\underline{CH_2}$), 132 (Si—$\underline{CH}$=CH$_2$), 125 ($\underline{CF_3}$), 124 ($\underline{CH}$=C in MPABI), 8.5 (SiCH$_2$), -1.5 (SiCH$_3$), 15–55 (Si—CH$_2\underline{CH_2}$CH$_2$—N, $\underline{CH_2}$CF$_3$ and the other carbons of MPABI).[21,25]

As a contrast, common vinyl-containing fluorosilicone (C-VFS) was prepared in accordance with the aforementioned process, except that HAPMS and MPA were absent and the loading of D_3F was adjusted to 72.2 g. The corresponding preparation scheme of C-VFS was shown Scheme 2, the NMR results of C-VFS are listed as following:

^{1}H NMR (300 MHz, CDCl$_3$, δ): 5.6–6.2 (Si—CH=CH$_2$), 2.0–2.3 (CH$_2$CF$_3$), 0.7–0.8 (Si—CH$_2$), 0–0.3 (Si—CH$_3$).[4]

^{13}C NMR (75 MHz, CDCl$_3$, δ): 125 (CH$_2\underline{CF_3}$), 26–27 ($\underline{CH_2}$CF$_3$), 8.5 (SiCH$_2$), -1.5 (SiCH$_3$).[29]
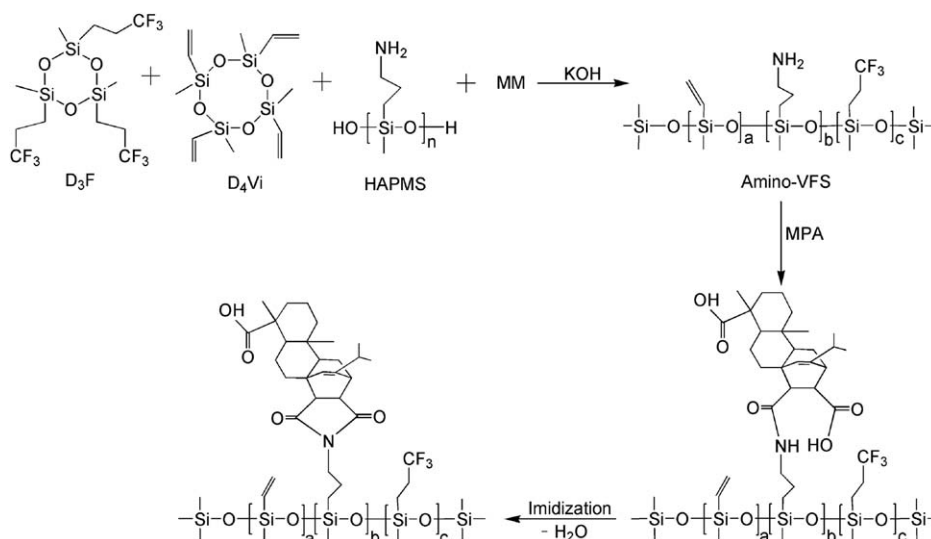
**SCHEME 1** Preparation of maleopimaric acid modified vinyl-containing fluorosilicone resin (MP-VFS).

Preparation of Fluorosilicone Rubber Sample P-FSR, C-FSR, and MP-FSR

In this article, the content of vinyl group in MP-VFS is equal to that in C-VFS, which is 6.3% and calculated form their reaction formulas. In order to evaluate the effect of MPABI on the properties of fluorosilicone rubber, different weight parts of VFS were blended with 100 weight parts of fluorosilicone gum, 36.4 weight parts of HDK®N20 and 7.2 weight parts of fluorosilicone oil in a vacuum kneader. After that, the mixing temperature was increased to 150 °C and kept at a pressure of 30 mmHg for 6 h. After being cooled to room temperature, with 100 parts of the obtained above mixtures, 0.5 parts by weight of DBPH were mixed uniformly using a two-roll. Thin sheets of 2 mm thickness were compression molded at 170 °C under a pressure of 10 MPa and post-cured at 200 °C for 2 h. All FSR samples were prepared in accordance with the aforementioned process.

P-FSR contained neither C-VFS nor MP-VFS, and was prepared as a contrast. C-FSR used C-VFS as the cross-linker, while MP-FSR used MP-VFS as the cross-linker. The needed parts and weight percent of VFS were listed in Table 1.

RESULTS AND DISCUSSION

In this study, modified by the natural rosin derivative MPA, MP-VFS was further used as a novel cross-linker to prepare MP-FSR. So the structure of MPA might affect the morphology, properties and application of MP-FSR.
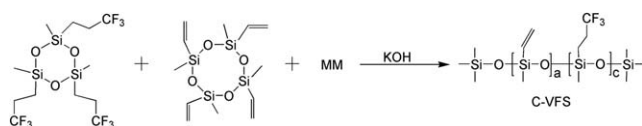
SCHEME 2 Preparation of common vinyl-containing fluorosilicone resin (C-VFS).

### Characterization of MP-VFS and C-VFS

With the great difference in molecular structure, MPA could not dissolve in fluorosilicone polymer to form a homogeneous solution. However, in this study, the obtained reaction product MP-VFS was homogeneous, which strongly demonstrated the formation of chemical bonding between MPA and fluorosilicone polymer.

In order to study the chemical grafting reaction, the chemical structure of C-VFS and MP-VFS were characterized by ^{1}H NMR and ^{13}C NMR, and the obtained spectra were presented in Figures 1 and 2. The NMR spectra of MP-VFS were more complex than C-VFS. However the characteristic peaks of MPA based imide heterocycle (MPABI) could be observed in the ^{1}H NMR and ^{13}C NMR spectra. These signals, especially the peaks of CH=C and O=C—N—C=O, strongly proved that MPABI had been successfully grafted onto the side chain of fluorosilicone polymer, which was illustrated in Scheme 1.

With potassium hydroxide as the catalyst, the aminopropyl vinyl-containing fluorosilicone resin (amino-VFS) was firstly

TABLE 1 Weight Parts and Weight Percent of Vinyl-Containing Fluoroslicone Resin (VFS) used in the Preparation of FSR

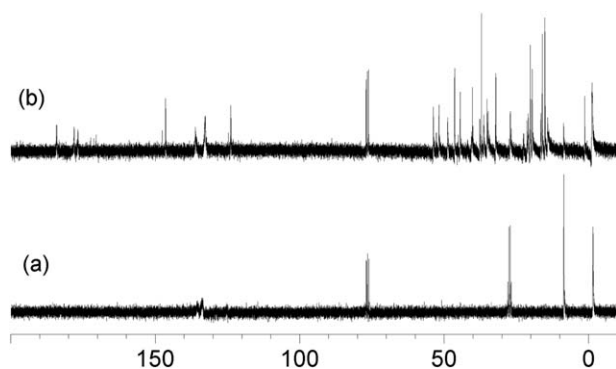| Sample	MP-VFS		C-VFS	
	Parts	wt %	Parts	wt %
P-FSR	0	0	0	0
C-FSR1	0	0	1.5	1.0
C-FSR2	0	0	3.0	2.0
C-FSR3	0	0	4.5	3.0
C-FSR4	0	0	6.0	4.0
MP-FSR1	1.5	1.0	0	0
MP-FSR2	3.0	2.0	0	0
MP-FSR3	4.5	3.0	0	0
MP-FSR4	6.0	4.0	0	0
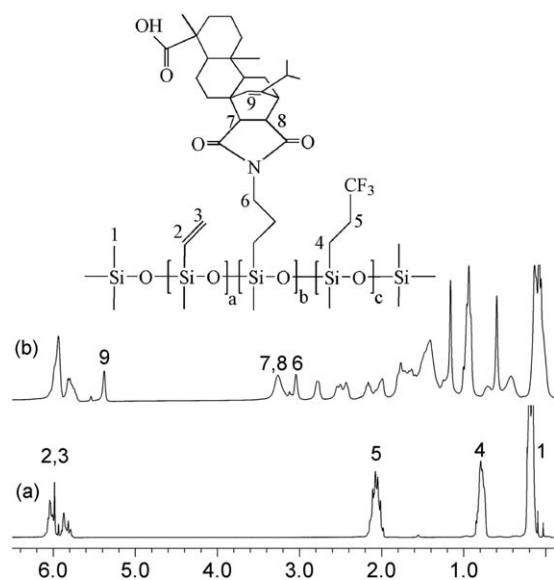
FIGURE 1 ^{1}H NMR spectra of C-VFS (a) and MP-VFS (b).
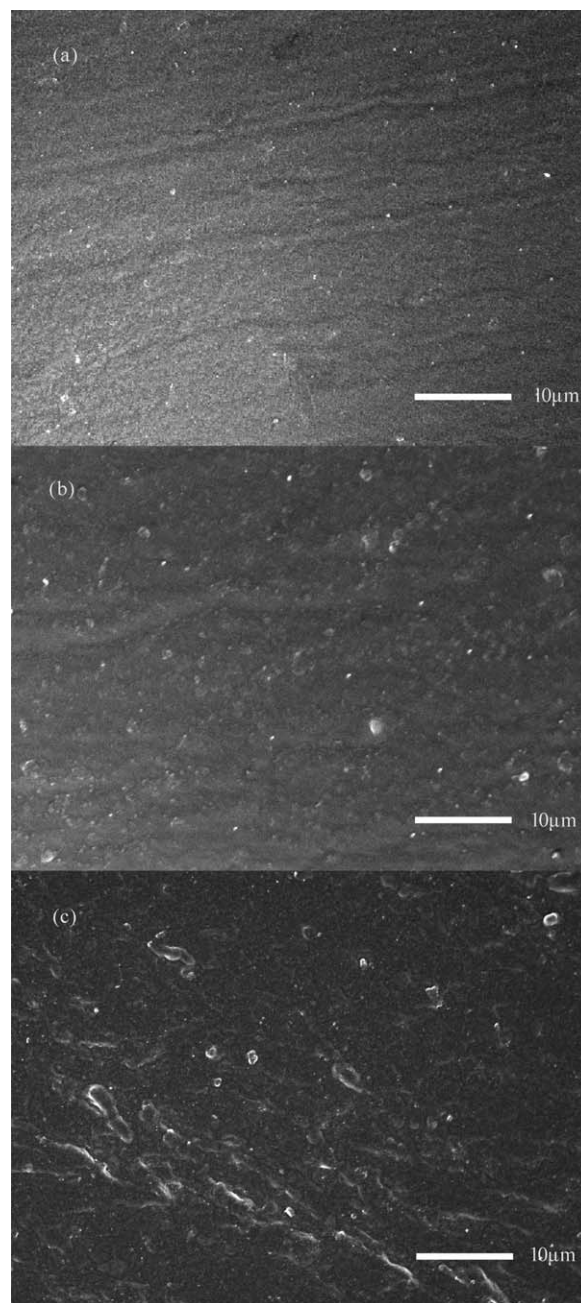
preprared from the anionic copolymerization of D_3F, D_4Vi, and HAPMS, while MM was used as the terminating agent. Secondly, the primary amino group(-NH$_2$) could easily react with acid anhydride group (O=C—O—C=O),[19–21,25] and the amide formed from MPA and aminopropyl group. Finally, under high temperature (higher than 150 °C) and vacuum conditions, the cyclization of amic acid to imide (i.e., imidization reaction) was completed,[20,21] and then the MPABI heterocycle was grafted onto the side chain of vinyl containing fluorosilicone resin.

Morphologies Study

Since MPA is solid powder under usual condition and has more stronger polarity and rigidity than fluorosilicone gum, the structure transformation of anhydride to imide in maleopimaric acid further increased its polarity and rigidity. In theory, this difference in the polarity and rigidity would lead to the phase seperation between MPA based imide and fluorosilicone polymer, and MPABI-rich phase would be formed in the fluorosilicone rubber. Actually, the similar microphase separation phenomenon between imide segment and silicone
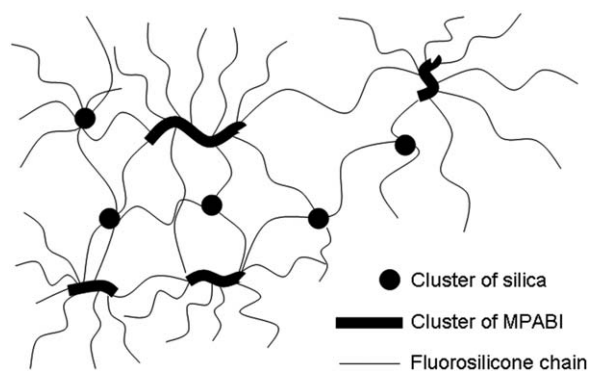

FIGURE 3 SEM images of (a) P-FSR; (b) C-FSR2; (c) MP-FSR2.

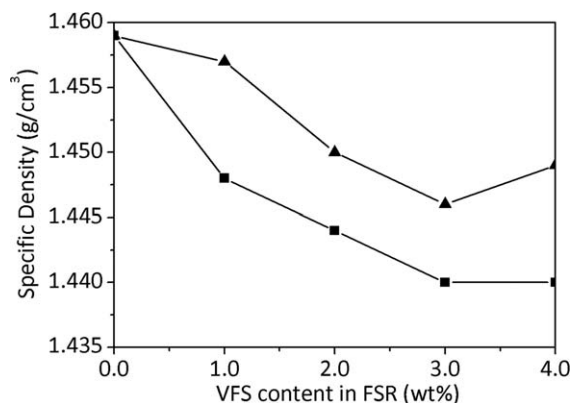segment had been observed by SEM in poly(methyltrifluoropropylsiloxane-b-imide) copolymer.[19]

In this study, SEM was used to study the micro-morphology of the new cross-section of MP-FSR. With the median value of MP-VFS loading, MP-FSR2 was selected as a representative sample while C-FSR2 and P-FSR were chosen as the comparative examples, and the obtained micrographs were showed in Figure 3. It could be found that the phase heterogeneity of C-FSR2 was stronger than P-FSR, which should be caused by the introduction of the cross-linker C-VFS, and MP-FSR exhibited the most serious microphase separation. The bright domains were dispersive and could be classified as

FIGURE 2 ^{13}C NMR spectra of C-VFS (a) and MP-VFS (b).

SCHEME 3 Dispersive phase structure of MP-FSR.

● Cluster of silica
▬ Cluster of MPABI
— Fluorosilicone chain

TABLE 2 Mechanical Properties of FSR

Sample	Tensile Strength (MPa)	Breaking Elongation (%)	Crosslinking Density (γ_e) (10^{-3}mol/kg)
P-FSR	9.2	202	12.8
C-FSR1	8.7	197	12.4
C-FSR2	8.2	177	13.1
C-FSR3	8.1	172	13.4
C-FSR4	8.1	168	13.7
MP-FSR1	8.8	203	12.3
MP-FSR2	8.7	210	11.8
MP-FSR3	8.2	205	11.4
MP-FSR4	7.9	200	11.3

followings: one was spherical and micron-sized, which should be the cluster of fumed silica; the other was belt-type, which was likely to be the MPABI-rich phase. The residual domain was dark and continuous, which should be the fluorosilicone polymer. The possible phase dispersion structure of MP-FSR was shown in Scheme 3. With the strong polarity of imide heterocycle, MPABI increased the cohesion energy of fluorosilicone rubber. Driven by this strong cohesion energy, MPABI tended to aggregate, and led to the microphase separation. The continuous phase was loose and soft fluorosilicone polymer phase, while the isolated and dispersive phases were dense and hard MPABI-rich phases and silica phases.

Effect of the above microphase separation on the free volume could be reflected by the change of rubber density, which was presented in Figure 4. It could be observed that the specific density of MP-FSR was less than C-FSR. So there was larger free volume among molecular chains of MP-FSR, which should be produced by the loosening of the continuous fluorosilicone polymer phase. That is to say, the appearance of the MPABI-rich phases in fluorosilicone rubber resulted in the density decrease and free volume increase of fluorosilicone polymer phase. When MP-VFS content exceeded 2%, the decline curve of specific density of MP-FSR slowed down, which indicated that the growth rate of free

volume in MP-FSR slowed down. As compared with C-FSR, the increase of free volume in MP-FSR will be beneficial for the improvement of its rebound resilience.[30,31]

Mechanical Properties

The aforementioned micro-morphology of MP-FSR would produce some special macroscopic property.[23] The mechanical properties of FSR with varying contents of VFS were presented in Table 2. The tensile strength of MP-FSR and C-FSR slightly decreases with the increasing content of VFS.Although the enhancement effect of MPABI on the tensile strength is unnoticeable, breaking elongation is significantly improved as compared with conventional cross-linker (C-VFS). When the VFS content does not exceed 2.0 wt %, MPABI have a great improvement on the tearing strength, rebound resilience and hardness. When the VFS content is 2.0 wt %, compared with C-FSR, the tensile strength of MP-FSR increases by 6.1%, breaking elongation by 18.6%, tearing strength by 23.5%, rebound resilience by 9.7%, and hardness by 4.6%. The improvement of mechanical properties should be due to the incorporation of polar MPABI, which led to the increase of cohesion energy (E_{coh}) in MP-FSR.[23,29]

However, after the VFS content exceeds 2.0 wt %, the mechanical properties decrease. Effects of MP-VFS on the rebound resilience, tearing strength and hardness of MP-FSR are respectively and clearly visualized in Figures 5–7. It can be found that the above three properties of MP-FSR present the parabolic trend, in which the maximum value occurs at about 2.0 wt %. This is an very interesting phenomenon and maybe have a correlation with the microphase separation and crosslink density of MP-FSR.[29,31]
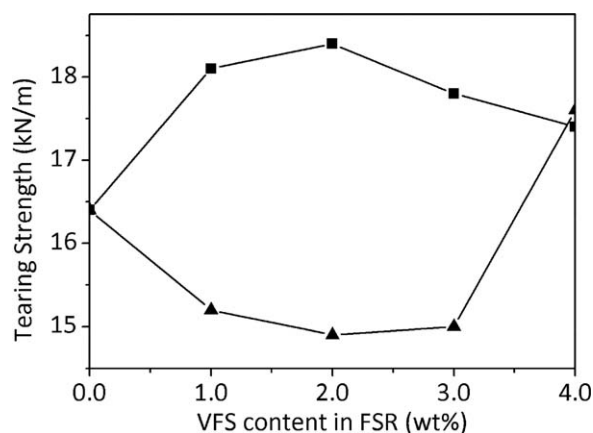
Data obtained from mechanical analysis could be used to study the average crosslink densities (γ_e) of vulcanized fluorosilicone rubber,[16] which were calculated according to eq 1 and presented in Table 2. It was noted that γ_e of MP-FSR decreased with an increase in the MP-VFS loading, or the content of MPABI, while that of C-FSR showed an opposite trend. It seemed that MPABI could inhibit the vulcanization
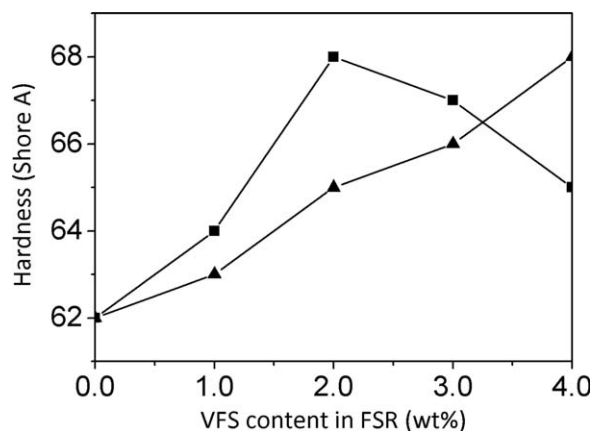

FIGURE 4 Effect of VFS on the specific density of FSR (-▲- C-FSR, -■- MP-FSR).
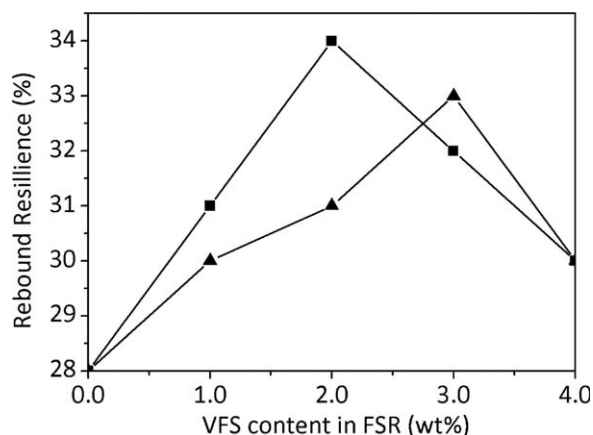
FIGURE 5 Effect of VFS on the rebound resilience of FSR (-▲-
C-FSR, -■- MP-FSR).

FIGURE 7 Effect of VFS on the hardness of FSR (-▲- C-FSR, -
■- MP-FSR).

of fluorosilicone rubber, which was a type of free radical polymerization initiated by DBPH, because it had been reported that rosin acid contained conjugated double bonds and could inhibit the free radical polymerization.[29,32] In this study, MPABI was synthesized from MPA, which was the Diels-Alder adduct of rosin acid and maleic anhydride.[24] So it was not difficult to understand that MP-VFS contains trace amounts of rosin acid.[29]

Because E_{coh} could resist the tearing rupture and increase the hardness, it seemed that both hardness and tearing strength of MP-FSR tended to have closer relation with the sum of γ_e and E_{coh} ($\gamma_e + E_{coh}$).[31] With the increase of MP-VFS content, MP-FSR's E_{coh} increased, while its γ_e showed an opposite trend. Mathematically, there was a possibility that the maximum value of their sum would occur at 2 wt % (e.g., γ_e could be represented by the monotonic increasing function $f_1(x) = l - m \cdot e^{(n-x)}$ where e was the natural constant and the other constants l, m, $n > 0$; E_{coh} could be represented by the monotonic decreaseing function $f_2(x) = a \cdot b^x$ where the constants a, $b > 0$; if $f(x) = f_1(x) + f_2(x)$, their sum $\gamma_e + E_{coh}$ could be represented by $f(x)$; when $l = 40$, $m = 2$,

$n = 3$, $a = 40$, $b = 0.815$, the relationship among γ_e, E_{coh} and their sum could be presented in Scheme 4). That is to say, the sum of γ_e and E_{coh} increased initially with the increasing content of MP-VFS, and then decreased when the content of MP-VFS exceeded 2 wt %. Effects of VFS content on γ_e, E_{coh}, and their sum were presented in Scheme 4. Hardness and tearing strength had a positive correlation with the sum of γ_e and E_{coh}, and therefore a parabolic trend could be observed in the hardness and tearing strength of MP-FSR (Figs. 6 and 7).

For the same reason, the rebound resilience of MP-FSR was correlated with both the free volume and crosslink density. When the MP-VFS was less than 2.0 wt %, the increase of rebound resilience was ascribed to the increasing free volume in MP-FSR, although the decreasing crosslink density played a minor and negative role. However, when MP-VFS content exceeded 2.0 wt %, there was a sharp slowndown in free volume growth, and the decreasing crosslink density replaced free volume as the major and negative role. As a

FIGURE 6 Effect of VFS on the tearing strength of FSR (-▲- C-
FSR, -■- MP-FSR).
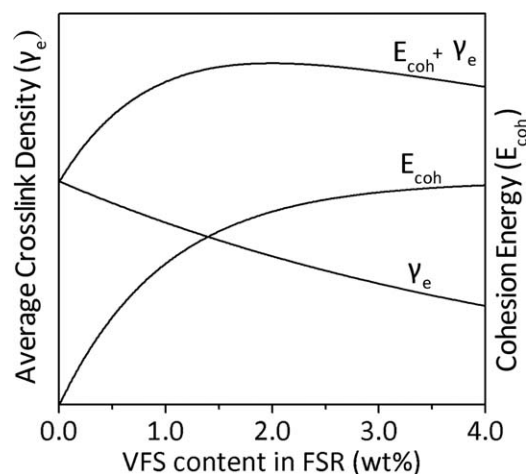
SCHEME 4 Effect of VFS content on the average crosslink density (γ_e), the cohesion energy (E_{coh}), and their sum ($\gamma_e + E_{coh}$) of MR-FSR.

TABLE 3 The Percent Change of Mechanical Properties Before and After Immersed in Oil

Sample	$\Delta N\%$ (1) (%)	$\Delta N\%$ (2) (%)	$\Delta N\%$ (3) (%)	$\Delta N\%$ (3) (%)
P-FSR	−45.0	−33.6	−58.5	−11.3
C-FSR1	−44.1	−33.9	−43.4	−12.7
C-FSR2	−43.1	−32.1	−43.6	−12.3
C-FSR3	−46.8	−35.9	−42.0	−10.6
C-FSR4	−47.4	−38.0	−41.5	−10.3
MP-FSR1	−42.2	−31.4	−45.3	−14.1
MP-FSR2	−45.9	−31.2	−46.2	−13.2
MP-FSR3	−47.9	−34.4	−46.6	−13.4
MP-FSR4	−48.7	−34.7	−47.1	−13.8

$\Delta N\%$ (1): the percent change of tensile strength, $\Delta N\%$ (2): the percent change of breaking elongation, $\Delta N\%$ (3): the percent change of tearing strength, $\Delta N\%$ (4): the percent change of hardness.

result, the rebound resillience presented the parabolic trend (Fig. 5).

In summary, incorporation of MPABI can effectively improve the mechanical strength of fluorosilicone rubber, such as hardness, rebound resillience, tearing strength and breaking elongation. Considering all above mechanical performance, 2.0% of MP-VFS should be chosen as the optimum operation point in this article.

Oil Resistance

Since fluorosilicone rubbers are mainly used as oil-resistance materials,[7,32] it is necessary to investigate the oil resistance property of MP-FSR. Their percent changes of mechanical properties were calculated according to eq. 2 and presented in Table 3. With the equal VFS content, the maximum difference between MP-FSR and C-FSR does not exceed 5%, except for the tearing strength. When the VFS content is at 2.0% (the optimum operation point), compared with C-FSR, the change rate of tensile strength of MP-FSR decreases by 2.8%, breaking elongation increases by 0.9%, tearing strength decreases by 2.6% and hardness decreases by 0.9%. It seems that MP-FSR has a little worse oil resistance than C-FSR. However, concerning the significant improvement of mechanical strength, there is a little decline of oil-resistance in MP-FSR. Additionally, MP-FSR has better oil-resistance in terms of change rates of breaking elongation. In sum, it could be concluded that MP-FSR behaves a little worse oil resistance than C-FSR, and still better than P-FSR.

High-Temperature Resistance

The thermal stability of FSR was measured by TG analysis. P-FSR, C-FSR2, and MP-FSR2 were chosen as the representative specimens, and their TG and DTG curves were shown in Figure 8. Before 450 °C, all specimens perform a similar thermal stability. Their obvious weight losses begin around 450 °C and the decomposition are complete by 600 °C. The values of T_{max} (the temperature corresponding to the
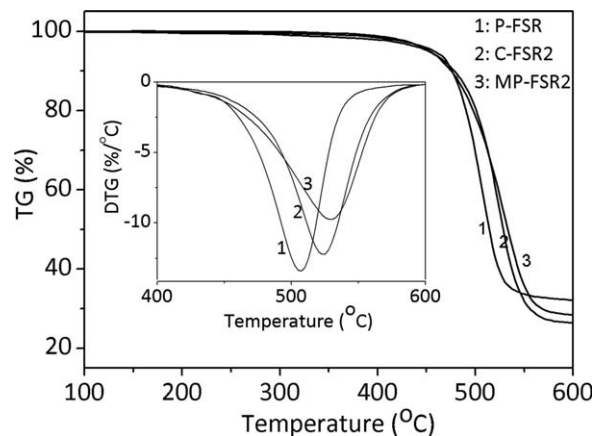

FIGURE 8 TG and DTG curves of P-FSR, C-FSR2 and MP-FSR2.

weight-loss rate-maximum in the DTG curves) are respectively 507.7 °C (P-FSR), 526.5 °C (C-FSR1), 523.6 °C (C-FSR2), 522.8 °C (C-FSR3), 522.1 °C (C-FSR4), 541.6 °C (MP-FSR1), 529.5 °C (MP-FSR2), 524.7 °C (MP-FSR3), and 512.7 °C (MP-FSR4). At the optimum operation point, after the incorporation of MPABI, the value of T_{max} is retarded by 5.9 °C. Based on the T_{max} comparation of FSR with the same VFS content, it could be concluded that MP-FSR shows better thermal stability than P-FSR and C-FSR. It is known that both phenanthrene ring[24,26,27] and imide heterocycle[19–22] have excellent thermal stability. Since both of them can be found in the structure of MPABI, the improvement of thermal stability of MP-FSR should be ascribed to the incorporation of MPABI. In sum, incorporation of MPABI could improve the thermal stability of fluorosilicone rubber.

Low-Temperature Resistance

The low-temperature resistance of FSR was investigated by DSC measurement. Considering that the range of usage temperature of ordinary fluorosilicone rubber is from −60 °C to 200 °C,[33] the measure temperature range was chosen from
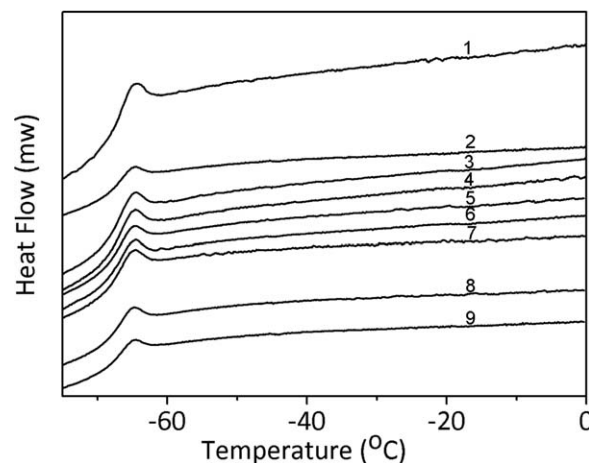
FIGURE 9 DSC curves of FSR (Line 1: MP-FSR2; Line 2: C-FSR2; Line 3: P-FSR; Line 4: MP-FSR4; Line 5: C-FSR4; Line 6: MP-FSR3; Line 7: MP-FSR1; Line 8:C-FSR1; Line 9: C-FSR3).

−75 °C to 200 °C in this article, whose results in the range from −75 °C to 0 °C were shown in Figure 9. All of the DSC curves show a similar change trend. Their glass transition temperatures (T_g) are respectively −67.3 °C (P-FSR), −67.6 °C (C-FSR1), −67.4 °C (C-FSR2), −67.5 °C (C-FSR3), −67.6 °C (C-FSR4), −67.6 °C (MP-FSR1), −67.4 °C (MP-FSR2), −67.7 °C (MP-FSR3), and −67.5 °C (MP-FSR4). All FSR in this article have the similar T_g value, which agrees with the reported value of −73 °C.[2] It means that MP-FSR exhibits the similar low-temperature-flexibility with P-FSR and C-FSR.

Additionally, in all DSC curves, there is no exo- or endothermic peak appeared from −60 °C to 200 °C. This shows that although the microphase separation occurs between MPABI segments and fluorosilicone polymer segments, the phase state of MP-FSR is stable in this wide temperature range, and there are no crystallizations, melting and other phase transformations occurred in MPABI-rich phases. In sum, it could be concluded that incorporation of MPABI has no obvious effect on the low temperature resistance of fluorosilicone rubber.

CONCLUSIONS

With maleopimaric acid (MPA) as imidization agent, a novel imide modified vinyl-containing fuorosilicone resin (MP-VFS) was firstly synthesized and characterized. This novel crosslinker MP-VFS, containing MPA based imide heterocycle (MPABI), was added into high temperature vulcanization (HTV) fluorosilicone rubber composition to prepare a series of MPA modified fluorosilicone rubbers (MP-FSR). Morphology, mechanical and oil-resistance properties, thermal properties, and low temperature resistance of MP-FSR had been studied by means of scanning electron microscope, universal tensile testing machine, thermogravimetric analysis, and differential scanning calorimetry. Microphase seperation in MP-FSR had been observed by SEM. Although the tensile strength was not significantly enhanced, the tearing strength, breaking elongation, rebound resilience, and hardness were effectively improved as compared with common fluorosilicone rubber. The oil-resistance and low-temperature resistance properties changed unobviously, while the thermal stability was enhanced due to the incorporation of MPABI.

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