Effects of —CH$_2$CH$_2$CF$_3$ on Properties of RTV Polysiloxane Rubber: Processability, Thermal Stability, and Oil/Solvent Resistance

Bo Li, Shuangjun Chen, Jun Zhang

Department of Polymer Science and Engineering, College of Materials Science and Engineering, Nanjing University of Technology, Nanjing 210009, People's Republic of China
Correspondence to: J. Zhang (E-mail: zhangjun@njut.edu.cn)

ABSTRACT: Room temperature vulcanizing fluorosilicone rubbers (FSRs) were prepared from polydimethylsiloxane (PDMS), vinyl fluorosilicone-oil (VFS-oil), and precipitated silica (PDMS/VFS/SiO$_2$). Rheological tests showed appropriate processing condition could be obtained when shear rate > 10 s^{-1}. Mechanical tests indicated that tensile strength and elongation at break were not much affected by VFS-oil and no decline was observed after being aged in 70 °C ASTM 1# oil. The —CF$_3$ group could not only increase oil-resistance, but also decrease surface energy, which were proved by ATR-FTIR and contact angle tests. The PDMS oil immersion tests showed that the higher the content of VFS-oil, the better oil resistance can be obtained. The solvent-resistance tests indicated that the VFS-oil improved resistance to nonpolar/low-polar solvent. TGA results showed that the increasing content of VFS-oil could slightly decrease FSRs' thermal stability but increase FSRs' residual mass ratio at 790°C. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39708.

INTRODUCTION

Room temperature vulcanizing (RTV) polydimethylsiloxane (PDMS) materials are widely used due to their superior properties in many fields, especially in the area of electronic sealing and potting technology.[1] Since some electronic components are used in oil environment, the good oil-resistance of the sealing materials is usually required. It is known that the nonpolar PDMS materials are poor resistant to some nonpolar oil such as a low molecular weight PDMS oil.[2] To overcome this drawback, many methods have been studied to improve the oil resistance of the PDMS materials.[3–5]

Commonly, the oil-resistance modifications of the RTV PDMS sealing materials could be classified by either physical or chemical methods. The physical method usually refers to addition of various fillers or coating of some hybrid inorganic/organic polymers so that the materials' swelling ratio to the oil or fuel could be reduced.[3] The chemical modification was generally achieved by grafting or blocking some functional groups to the PDMS chains. For example, —CN group and fluorine-containing group that have high polarity are usually used to substitute the —CH$_3$ group in the PDMS.[6–8] The fluorine-containing groups (—CH$_2$CH$_2$CF$_3$, etc.), could decrease the materials' surface energy,[9,10] and thus are commonly used to incorporate into the polysiloxanes to enhance the materials' resistance to both oils

and nonpolar solvents.[11] High temperature vulcanizing fluorosilicone rubbers (FSRs), which are containing of —CH$_2$CH$_2$CF$_3$, have been widely investigated in the past decades.[6,12,13] However, the RTV-type FSRs has been rarely reported.[14,15]

Polymer blending is an easy and effective method to develop new polymeric materials, since it combines the properties of different polymer components to overcome a particular drawback of a certain individual component.[16–19] Considering the fact that the prices of polysiloxanes or copolysiloxanes that contain the —CH$_2$CH$_2$CF$_3$ are very high,[7] ordinary vinyl terminated PDMS is usually incorporated for the purpose of saving cost.[13] Based on this, both a simple process and high efficiency of outputting products can be obtained. Besides, the properties of materials can be tailored by merely adjusting the ratio of polymer components.

In our previous work,[20] vinyl fluorosilicone oils (VFS-oil) that had random distribution of —(CH$_3$)Si(CH$_2$CH$_2$CF$_3$)O— (F unit) and —(CH$_3$)$_2$SiO— (D unit) were synthesized and characterized. In this article, the synthesized VFS-oil with moderate —CH$_2$CH$_2$CF$_3$ and Si—CH═CH$_2$ content (F/D = 3/7, vinyl content = 0.38 wt %) was chosen to blend with traditional RTV silicone rubber so that its solvent-resistance can be enhanced. What's more, the materials' oil resistance could be regulated by adjusting the dosage of the VFS oil, and the high
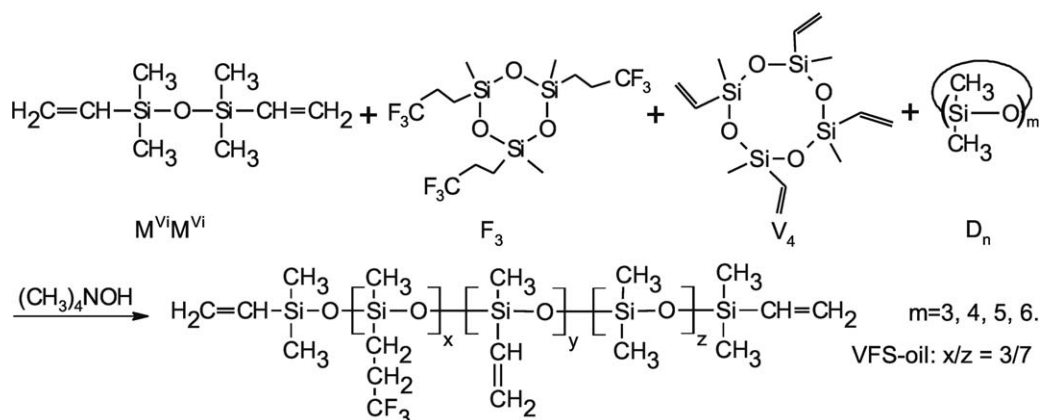
Scheme 1. Details for the polymerization of VFS-oil.

performance-to-price ratio materials could be obtained when the appropriate dosage of VFS was used. RTV FSRs with different dosages of VFS-oil were prepared in this study. The effect of VFS-oil on properties was investigated. The processability and mechanical properties were reported. The surface properties were studied by attenuated total reflection Fourier transform infrared (ATR-FTIR) and contact angle tests. The thermal degradation in inert environment was performed by thermogravimetic analysis (TGA). The oil resistance was also investigated.

EXPERIMENTAL

Materials

1,3,5-Tris(3,3,3-trifluoropropyl)-1,3,5-trimethylcyclotrisiloxane (F_3, purity: $> 99.5\%$) was obtained from Weihai New Era Chemical. A mixture of dimethyl cyclosiloxane (D_n, $3 \leq n \leq 6$, D_n content: $> 99.5\%$) was obtained from Huarun 1,3-divinyl-1,1,3,3-tetramethyldisiloxane ($M^{vi}M^{vi}$, purity: $> 99.5\%$) and 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (V_4, purity: $> 99.5\%$) were both supplied by Nanjing Kangmanling. The $(CH_3)_4NOH$ (25 wt % of water solution) used as a catalyst was supplied by National Pharmaceutical Group Chemical Reagent. All of these materials were used for the preparation of the VFS-oil (with random distribution of F and D units), and the details are shown in Scheme 1.

Vinyl-terminated PDMS (vinyl-terminated, $\eta_{25} = 1000$ mPa·s, vinyl group content $= 0.30$ wt %, number and weight average molecular weight were 21,487 and 34,146 g/mol, PDI $= 1.59$) was purchased from Huarun. Hydrogen-containing silicone oil (active hydrogen content $= 1$ wt %) used as a crosslinking agent was obtained from Dayi Inc. (Shandong, China). The platinum complex (laboratory-made, Pt content: 0.30 wt %) catalyst was synthesized by the method reported previously.[21] Precipitated silica (trademark: FINE-SIL 515) was supplied by Wanzai Chemical (Jiangxi, China). The PDMS oil (methyl-terminated, $\eta_{25} = 500$ mPa s), which was used for oil resistance test, was purchased from Shaoxing Nuoyu Silicone Material.

Table I. Formulation for the Preparation of the VFS-Oil

Materials	F_3	D_n	V_4	$M^{vi}M^{vi}$	$(CH_3)_4NOH$
Dosage (phr)	88	100	0.588	1.762	0.188

Synthesis of VFS-Oil

D_n, F_3 (feed ratio: $-CH_2CH_2CF_3/Si = 3/10$), $M^{vi}M^{vi}$, V_4, and $(CH_3)_4NOH$ were mixed (Table I). The mixture was heated to $100 \pm 2^\circ C$ under the nitrogen atmosphere. The reaction was kept for 4.5 h and then the system was quickly heated to $160 \pm 2^\circ C$ to remove the $(CH_3)_4NOH$ (about 1 h). Finally, the cyclic oligosiloxanes were removed by reducing the pressure of the system (< 1 kPa) at $180–200^\circ C$.[20] The number and weight average molecular weight of the VFS-oil were 18,825 and 32,559 g/mol, respectively, while the PDI was 1.73 (Obtained by GPC).

Sample Preparation

The compositions of the mix gums (without Pt catalyst) and polysiloxane rubbers are listed in Table II. The PDMS, VFS-oil, SiO_2, and appropriate Hydrogen-containing silicone oil (molar ratio of $H-Si/CH_2=CH-Si = 1.3/1$[22]) were blended with different ratios as shown in Table II, and all of the six samples were ground with a three-roll mill (ST65/150, Changzhou Zili, China) at room temperature for three times. A small amount of each mixture (≈ 2 mL) was separated subsequently, and all the samples were numbered as MG0/10 (MG is short for mixed gum), MG1/9, MG2/8, MG3/7, MG4/6, and MG5/5, respectively, which were used for the rheological tests. Then the Pt complex catalyst (20 ppm of the sample weight) was added into each mixed gum, and the mixtures were stirred and poured into a polytetrafluoroethylene mould separately. After eliminating the air bubbles, they were cured at room temperature ($25^\circ C$) for more than 24 h (the properties tests were performed after a week).

Characterizations and Measurements

GPC analysis was performed in a PL-GPC-120 apparatus (Polymer Laboratories, Britain), and its system was calibrated using narrow polydispersity polystyrene standards. ^{1}H NMR analysis of synthetic VFS-oil was conducted with a Bruker DRX500-MHz nuclear magnetic resonance spectrometer (Bruker, Switzerland), and it was carried out under the conditions of room temperature and CDCl_3. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane as an internal standard. ATR-FTIR spectra were obtained with a spectrometer of Nicolet iS5 (Thermo Fisher, America). Each spectrum was recorded by performing 32 scans between 4000 and 400 cm^{-1}, and the resolution was 4 cm^{-1}. Contact angles were determined using a

Table II. Compositions of the Different Mixed Gums (MG) and RTV Polysiloxane Rubbers

Sample	VFS-oil (phr)	PDMS-oil (phr)	Molar ratio of VFS/PDMS	SiO$_2$ (phr)	Pt catalyst (ppm)
MG0/10	0	100	0/10	10	–
SR	0	100	0/10	10	20
MG1/9	10	90	1.14/9	10	–
FSR1/9	10	90	1.14/9	10	20
MG2/8	20	80	2.28/8	10	–
FSR2/8	20	80	2.28/8	10	20
MG3/7	30	70	3.42/7	10	–
FSR3/7	30	70	3.42/7	10	20
MG4/6	40	60	4.57/6	10	–
FSR4/6	40	60	4.57/6	10	20
MG5/5	50	50	5.71/5	10	–
FSR5/5	50	50	5.71/5	10	20

DSA 100 drop shape analysis system (Krüss, Hamburg, Germany) at room temperature. The test liquid (2.0 μL of deionized water and diiodomethane) was dropped onto the sample surfaces from a needle tip, and the result was recorded after 30 s. Each value given below was the average of at least three measurements, with an error of $\pm 2°$. Thermogravimetric (TG) analysis was carried out in a TGA (Waters TA, Q50) in a nitrogen flow (20 mL/min). Each scan was programmed from 25 to 800°C with a heating rate of 20°C /min.

Rheological Measurement. A rotational rheometer instrument of HAAKE Rheo-Stress 600 was used to measure the rheological properties of the mixed gums. The scan ranges of shear rate ($\dot{\gamma}$) and temperature were 0.1–100 s^{-1} and 25–80°C, respectively. The measurements were conducted by using a set of 35 mm diameter parallel plates with a sample thickness of 0.7–0.9 mm, and the preshear of the sample was carried out before the test.

Mechanical Properties Tests. The cured rubber samples were manufactured as standard dumbbell-shape pieces and measured by CMT-5254 universal testing machine (Shenzhen Sans Test Machine, China), with an extension rate of 500 mm/min at room temperature, according to ISO 37-1994. Shore A hardness was recorded according to ISO 868. Mechanical properties after being immersed in the ASTM 1# oil at 70°C for 24 and 72 h were also investigated.

Dynamical Mechanical Analysis (DMA) Tests, which were used to obtain storage modulus of the samples, were conducted in a rheometer (MCR302, AntonPaar, Austria) that has a function of DMA tests. Each test was scanned in a torsion mode with a frequency of 1 Hz in the temperature range from 25 to 35°C at a heating rate of 3°C/min. The dimension of the each specimen was 30 × 6 × 2 mm.

Crosslinking Degree Test. Crosslinking densities of the samples were measured by swelling method, and the toluene was used as solvent.[23] The crosslinking degree was calculated using the Flory-Huggins equation.[24]

$$V_e = \frac{-N_A \left[\ln\left(1 - V_R\right) + V_R + \chi_1 V_R^2\right]}{V_1\left(V_R^{1/3} - V_R/2\right)} \quad (1)$$

where V_e is the crosslinking density per unit volume, V_1 is the molar volume of the solvent (toluene), and V_R is the volume fraction of the polymer in the swollen specimens. The Flory-Huggins interaction parameter χ_1 was set to be 0.45.[25]

Solvent Resistance Test. The acetone, ethyl acetate, normal heptane, and gasoline were chosen as the solvents. Each sample with the weight about 2 g was immersed in the solvents at 30°C for 72 h. The mass changes of each sample swelled in the solvents were detected ($\Delta M = (m_2 - m_1)/m_1$, where m_1 and m_2 are the mass of the specimens before and after the tests).

Oil Resistance Test. Dumbbell-shaped test specimens were immersed in ASTM 1# oil at 70°C for 24 and 72 h, respectively (according to ASTM D471-1998). Then they were used for the mechanical tests, and the results were used to determine the polysiloxane rubbers' oil resistance to the ASTM 1# oil. In addition, each sheet of the samples was cut into the size of 25 × 25 × 2 mm, and they were immersed in the ASTM 1# oil (70°C for 24 and 72 h) separately, and the PDMS oil (500 mPa s) for 12 days with 3-day intervals at room temperature. Then both of the percent change in mass (ΔM) and volume (ΔV) of the samples were detected and they were used to evaluate the oil resistance of the samples. ($\Delta M = (m_2 - m_1)/m_1$, where m_1 and m_2 are the masses of the specimens before and after the immersion; $\Delta V = (v_2 - v_1)/v_1$, where v_1 and v_2 are the volumes of the specimens before and after the immersion.) The tests were recorded according to ISO-1817-2005.

RESULTS AND DISCUSSION

^{1}H NMR of Synthetic VFS-Oil

According to our previous report,[20] the distribution of the F and D unit in the main chain of the synthetic VFS-oil was random (This could be certified by the split of the Si—CH$_3$ signal peak). In this work, the ^{1}H NMR spectrum of VFS-oil is shown in Figure 1. And the peaks at 0.05–0.2 ppm (—CH$_3$),[26] 0.760 ppm (—CH$_2$CH$_2$CF$_3$), and 2.087 ppm (—CH$_2$CH$_2$CF$_3$)[14,27] could be observed. The signal in the range of 5.6–6.2 ppm, which could be attributed to the CH$_2$=CH—Si,[28] is not as obvious as other peaks. Thus, the curve of this range was enlarged and the detail was shown over the main spectrum. The calculation of the vinyl content was based on the integral area ratio of the proton peak. Setting the integration of Si—CH$_3$ peak as standard (100), other peaks' integrations are 11.36 (0.760 ppm, —CH$_2$CH$_2$CF$_3$), 11.37 (2.087 ppm, —CH$_2$CH$_2$CF$_3$), and 0.85 (5.6–6.2 ppm, Si—CH=CH$_2$), respectively. The content of vinyl was calculated according to these integrations and it was 0.38 wt %. In addition, the copolymerization ratio of the F/D was calculated out and it was 2.88/7.00 (—CH$_2$CH$_2$CF$_3$/Si = 2.91/10). In this work, the comprehensive properties of the addition-type RTV polysiloxane rubbers that were blended with the self-synthetic VFS-oil were explored.

Rheological Tests

Rheological tests were used to evaluate the processability.[11] The apparent viscosities (η_a) of the mixed gums at different $\dot{\gamma}$ were shown in Figure 2(A), while Figure 2(B) showed the η_a (shear
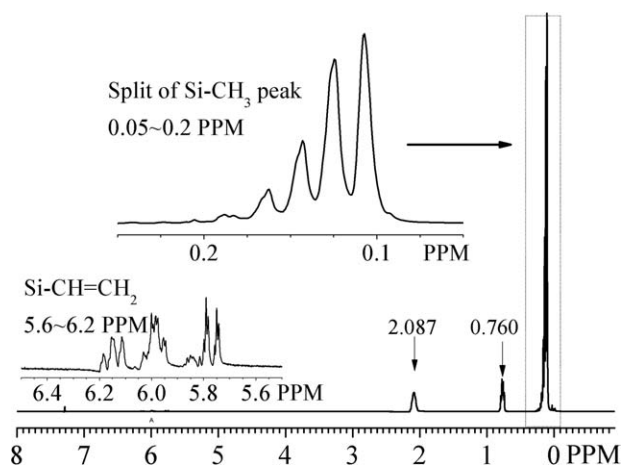
Figure 1. ^{1}H NMR spectrum of the VFS-oil.

rate is 1 s^{-1}) at different temperatures. The apparent shear-thinning character of the mixed gums with higher VFS-oil content could be observed in Figure 2(A), while the temperature-sensitive character was exhibited in Figure 2(B). As shown in Scheme 1, there was about 30 mol % (29.1 mol % calculated by ^{1}H NMR) of F unit in the VFS-oil, and the —CH$_2$CH$_2$CF$_3$ is so large that it exerted an increasing steric-hindrance effect, which hampered the motion of the VFS-oil chain.[29] Besides, the —CH$_2$CH$_2$CF$_3$ is a polar group due to the presence of fluorine,[30] so the force of interaction between the —CH$_2$CH$_2$CF$_3$ group and the Si—OH group on the SiO$_2$ particles' surface was higher than that between PDMS chain and SiO$_2$. Hence, the sample with higher VFS-oil content showed the more obvious "structural effect," which is responsible for the characters of shear-thinning and temperature-sensitivity.

As shown in Figure 2(A), the η_a of the mixed gums turned out to be much close when the $\dot{\gamma}$ was higher than 10 s^{-1}. The decrease in η_a would be helpful in the manufacturing procedure, since higher viscosity of polymers would decrease the outputting efficiency of products. Thus, it could be concluded that appropriate process condition could be obtained when $\dot{\gamma} > 10$ s^{-1}.

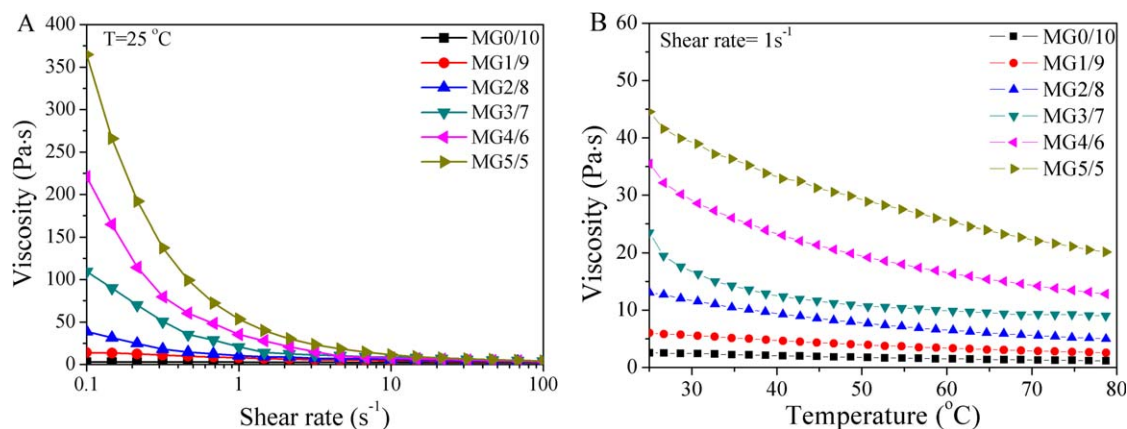## Mechanical Properties

The mechanical properties of the polysiloxane rubbers before and after being immersed into the ASTM 1# oil at 70°C were determined. And the results were shown in Figures 3 and 4. The tensile strength of the control samples were changed in the range of 1.4–1.8 MPa. Commonly, the tensile strength of the neat PDMS (without silica and VFS) was just about 0.4 MPa.[31] The nature of this brittleness makes the tests on the samples hard to be carried out, since the samples are easily fractured even before the tests. However, the strength of the samples was well enhanced by adding silica, based on which the mechanical properties tests could be performed successfully. No significant decline in tensile strength was observed with the VFS content increasing, which indicated the good compatibility of the VFS copolymer and PDMS.[15]

After being immersed in the ASTM 1# oil, the tensile strength of each sample was just slightly decreased. This suggested that the samples have good resistance to the ASTM 1# oil. Similar trends could also be observed with regard to elongation at break [see Figure 3(B)]. In sum, all of the three curves exhibited a slight decline as the VFS-oil content increased. Compared with the control samples, the hardness presented in Figure 4 was also slightly decreased after the ASTM 1# oil immersion. The effect of the ASTM 1# oil on the samples could be responsible for the decline in the hardness. However, the high retention rate of tensile strength and elongation at break illustrated that the ASTM 1# oil just penetrated into the surface layer, while exerted less influence in deep layer of the samples.[13] Therefore, the samples' resistance to the ASTM 1# oil was good.

To detect the difference of the storage modulus of the samples, the DMA tests were performed at room temperature (30°C) and the results were list in Table III. The storage modulus was increased with the increasing VFS content. This might be attributed to the higher molecule chains' rigidity caused by the —CH$_2$CH$_2$CF$_3$ groups, based on which higher modulus could be gained. The DMA tests results illustrated that the samples' flexibility was decreased by incorporating VSF-oil.
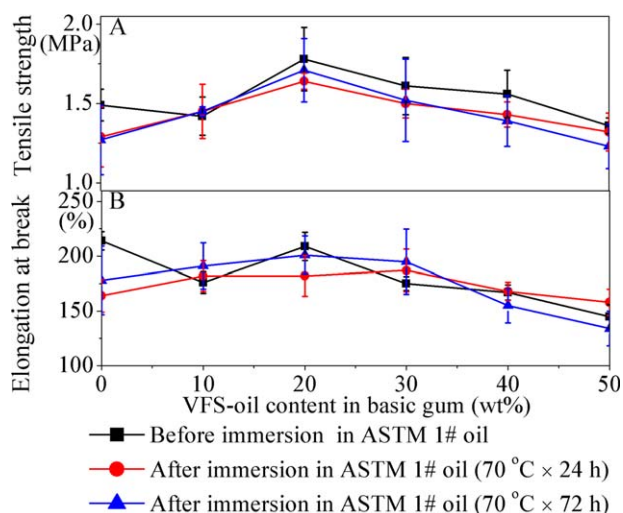

Figure 2. Apparent viscosities (η_a) of the mixed gums at different shear rates (γ') and temperature (T). A: $\eta_a - \gamma'$; B: $\eta_a - T$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3. Tensile strengths and elongation at break of the SR (VFS-oil content in basic gum: 0 wt %), FSR1/9 (10 wt %), FSR2/8 (20 wt %), FSR3/7 (30 wt %), FSR4/6 (40 wt %), and FSR5/5 (50 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Crosslinking Density

As shown in Figure 5, the highest crosslinking density was obtained when the VFS-oil content reached 20 wt % in the basic gum (FSR2/8). However, the difference in crosslinking density between different samples was not obvious. In spite of that the vinyl content of the VFS-oil (≈ 0.38 wt %) was higher than that of PDMS (≈ 0.30 wt %), not all of the Si—CH$=$CH$_2$ participate in the crosslinking reaction. Some of the vinyl groups, which is connected with the Si near the F unit, could not be involved in the hydrosilylation reaction due to shielding effect exerted by the —CH$_2$CH$_2$CF$_3$. Thus, the samples' crosslinking degrees were not much changed as VFS-oil content increased. This result was consistent with the aforementioned results of the tensile strengths, elongation at break, and hardness.
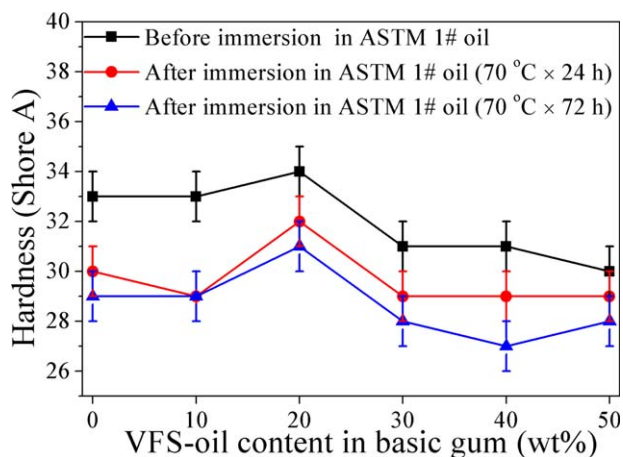
Table III. Storage Modulus of the Samples at 30°C

Sample	Storage modulus (kPa)
SR	147
FSR1/9	391
FSR2/8	544
FSR3/7	667
FSR4/6	860
FSR5/5	935

Oil and Solvent Resistance

The ΔM and ΔV of the samples, which were immersed in ASTM 1# oil (70°C for 24 and 72 h), are presented in Figure 6. Both of the ΔM and ΔV were <3% and were not significantly changed as VFS-oil content increased. It is interesting to notice that ΔM and ΔV of the samples, which was immersed for 24 h was higher than that of the samples immersed for 72 h. The reason for this unexpected phenomenon could be as follows: all of the changes in mass and volume were too low (even <3%), and thus the residual oil on the surface of the samples would significantly affect the testing results, even though the oil on the samples' surface had been sufficiently cleaned before the measure. The relative high standard deviation could be attributed to abnormal result. The low ΔM and ΔV indicated samples' good resistance to the ASTM 1# oil. However, when it comes to the samples that were immersed in PDMS oil (for 3, 6, 9, and 12 d, at room temperature), the ΔM and ΔV (caused by PDMS oil) were much higher (see Figures 6 and 7). This was obvious for the SR, FSR1/9, and FSR2/8, which have relative lower VFS-oil content and are therefore more vulnerable to the PDMS oil. With the increasing VFS-oil content, the ΔM and ΔV decreased as a function of the immersion time. For instance, when the VFS-oil content increased to 50 wt % (FSR5/5), the ΔM and ΔV were only half of SR's. It is known that the polarity of VFS chain is higher than that of PDMS chain, due to the presence of fluorine.[32,33] Consequently, the samples containing higher
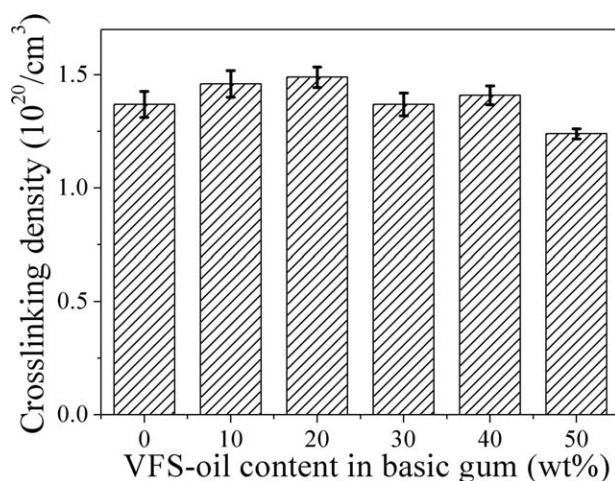

Figure 4. Hardness of SR (VFS-oil content in basic gum: 0 wt %), FSR1/9 (10 wt %), FSR2/8 (20 wt %), FSR3/7 (30 wt %), FSR4/6 (40 wt %), and FSR5/5 (50 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. Crosslinking degrees of the SR (VFS-oil content in basic gum: 0 wt %), FSR1/9 (10 wt %), FSR2/8 (20 wt %), FSR3/7 (30 wt %), FSR4/6 (40 wt %), and FSR5/5 (50 wt %).
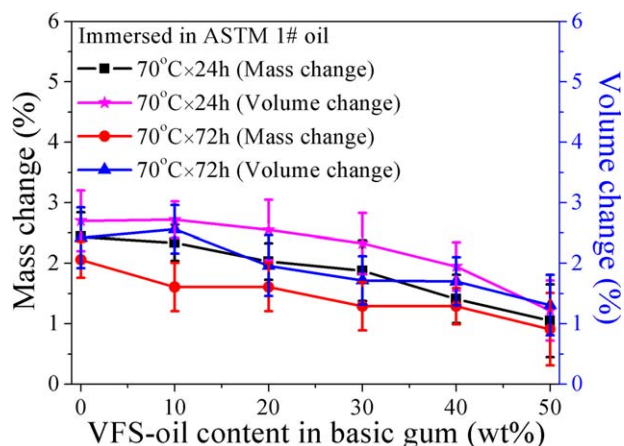
Figure 6. ΔM and ΔV of SR (VFS-oil content in basic gum: 0 wt %), FSR1/9 (10 wt %), FSR2/8 (20 wt %), FSR3/7 (30 wt %), FSR4/6 (40 wt %), and FSR5/5 (50 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

VFS-oil content were more resistant to the attack of the nonpolar PDMS oil, which reduced the ΔM and ΔV.

The solvent swelling experiments were performed to evaluate the solvent resistance of the samples. The acetone, ethyl acetate, normal heptane, and gasoline were used. The polarity of them gradually decreased in the following order: acetone > ethylacetate > normal heptane > gasoline. The ΔM of the samples swelled in the solvents for $30°C \times 72$ h are listed in Table IV. When the VFS-oil content in the VFS/PDMS blends was increased, the ΔM_1 that is corresponded to acetone increased from 22.8 to 51.7 wt %. However, it is interesting to note that ΔM were decreased with the increasing VFS content under the condition of being swollen in aliphatic solvents. This difference indicated the samples' good resistance to acetone and poor resistance to aliphatic solvents. This is consistent with results of the literature.[2]

Different molecule polarity could be responsible for such a difference. $-CH_2CH_2CF_3$ in VFS macromolecule chain is more polar than that of PDMS chain. The polarity of the acetone is

Table IV. Swelling Ratio of the Samples

	Swelling ratio (%, 30°C × 72 h)			
Sample	Acetone (ΔM_1)	Ethyl acetate (ΔM_2)	Normal heptane (ΔM_3)	Gasoline (ΔM_4)
1	22.8	135	228	235
2	29.0	130	214	223
3	35.9	125	190	195
4	39.4	117	160	171
5	45.4	124	149	157
6	51.7	125	144	154

the highest within the four solvent, so the samples' resistance to the acetone decreased as the VFS content increased. PDMS chain is commonly classed as a nonpolar macromolecule. Thus, the low-polar solvents, including normal heptane and gasoline, were easier to permeate the nonpolar samples, which in turn significantly decreased the swelling ratio (ΔM_3, ΔM_4) of the samples as VFS-oil content increased.

To further verify the contribution of the difference in polarity, the surface energy of each samples was determined from the static contact angles of distilled water and diiodomethane according to the Owens and Wendt method,[34] and the results were presented in Table V. As the VFS-oil content increased, the surface energy was decreased as well as ΔM and ΔV (immersion in PDMS oil) did. As literature reported,[35] the fluorine compounds generally have relatively low surface energy. This is especially obvious for those materials containing $-CF_3$ group, since the $-CF_3$ group has the lowest surface free energy among the groups of $-CH_2$, $-CH_3$, $-CF_2$, and $-CF_2H$.[35,36] Since VFS-oil contains $-CH_2CH_2CF_3$, incorporating VFS-oil effectively reduced the surface energy of the polysiloxane rubbers. This is also of great benefit to the samples' oil resistance. It should be pointed out that the value of the surface energy of FSR5/5 was extraordinary high. Perhaps the high surface tension might be related to its roughness of surface morphology. In other words, the high roughness of the surface rather than the nature of
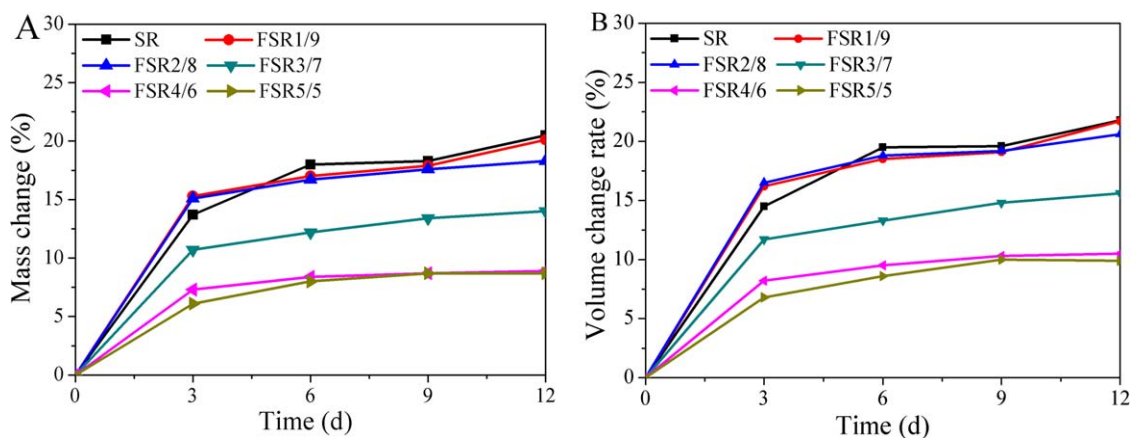

Figure 7. ΔM and ΔV of the samples after the PDMS oil immersion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Contact Angle and Surface Energy of Polysiloxane Rubbers

Sample	Contact angle (°)		Surface energy (mJ/m^2)
	Water	Diiodomethane	
SR	102.4	70.0	22.99
FSR1/9	106.4	71.5	22.05
FSR2/8	107.4	73.4	21.00
FSR3/7	110.8	75.3	19.97
FSR4/6	114.6	81.6	16.69
FSR5/5	128.3	101.6	8.19

materials contributed to the high surface tension. Similar results are also reported in a previous publication.[37]

ATR-FTIR Analysis

The ATR-FTIR spectra are exhibited in Figure 8, and the typical water drop pictures of the contact angle test are presented next to the spectrum. In this article, the peak at 1020 cm^{-1} was selected as an internal reference to erase the dosage effect of samples. As reported in the literature,[38,39] the strong absorption band from 1130 to 1000 cm^{-1} should be attributed to the Si—O—Si asymmetric stretching vibration. The main absorption peaks at 2963, 1261, and 795 cm^{-1} could be assigned to the —CH$_3$, structural vibration of Si—CH$_3$ and rocking of —CH$_3$, respectively. With respect to the peak at about 1209 cm^{-1}, which increased gradually with the increasing VFS-oil content, it should be attributed to the characteristic absorption of —CF$_3$.[38] The higher ratios between the height of the peaks at 1209 and 1020 cm^{-1} (h_{1209}/h_{1020}) indicated the increase in the —CF$_3$ on the samples' surfaces. And the increase in —CF$_3$ contributed to the decline in the surface energy, which was consistent with the change in contact angle. Therefore, the high resistance to the PDMS oil was obtained.

Thermal Stability

The thermal stability and residual mass were obtained by TG analysis and the results are presented in Figure 9. As the VFS-
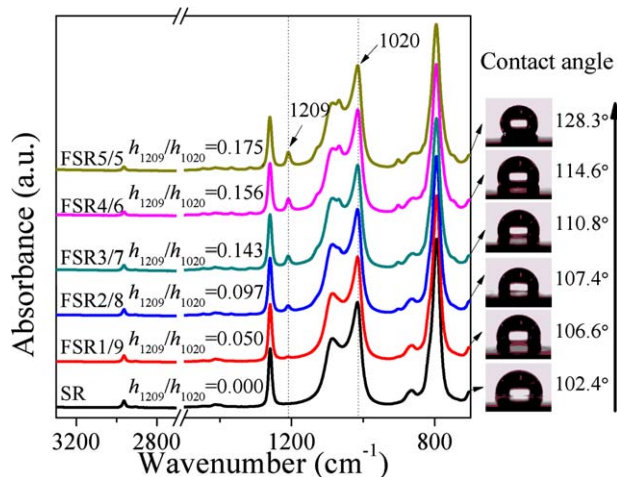

Figure 8. ATR-FTIR spectra of the samples and the contact angle with water drop. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
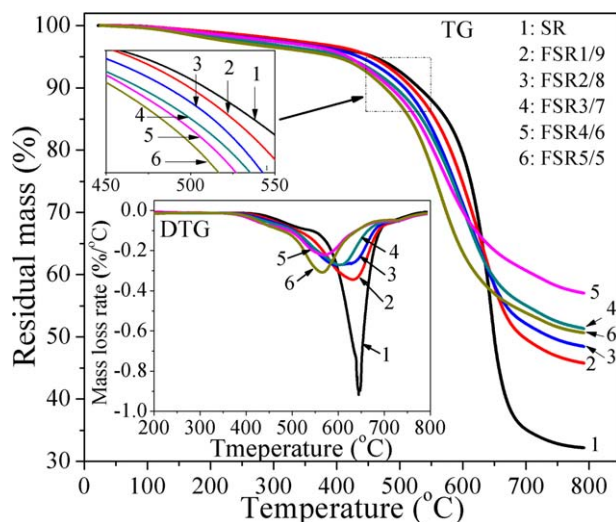

Figure 9. TG and DTG curves of the polysiloxane rubbers performed in N$_2$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

oil content increased, the thermal stability of the samples seemed to decrease, since the T_{10} (the temperature corresponding to the mass loss = 10%) of the SR, FSR1/9, FSR2/8, FSR3/7, FSR4/6, and FSR5/5 were 530.9, 519.8, 508.5, 494.5, 486.0, and 477.0°C, respectively. While the residual mass ratio (at 790°C) increased gradually as the VFS-oil content increased (SR: 32.2%, FSR1/9: 45.8%, FSR2/8: 48.5%, FSR3/7: 51.4%, and FSR4/6: 57.1). While the residue mass ratio of FSR5/5 (50.7%) was intermediate between that of FSR4/6 and that of FSR2/8. Thus, it could be predicted that the addition of VFS-oil was helpful in the mass residual ratio.

According to extensive investigations about the degradation of the PDMS materials,[40] the cyclosiloxanes were usually formed from the random scission reaction in the degradation of the PDMS under the condition of inert atmosphere and increasing temperature.[41] Meanwhile, there were also small amounts of methane and trace of linear oligomers in the heating process.[42] As shown in Scheme 2, when all of the X, X$_1$, X$_2$, and X$_3$ stand for the —CH$_3$, the degradation mechanism of PDMS could be described by the eq. (1) in Scheme 2. If we assume that the degradation only follows mechanism I, and the cyclosiloxanes were volatile at high temperature (>300°C), the calculated residual mass of PDMS should be only 9.1% (10 phr SiO$_2$ was incorporated in per 100 phr basic gum, and 10/110 = 9.1%). However, the experimental value is 32.2 wt %, which is >9.1 wt %. This indicates that some other decomposing mechanism also exist in this system. According to mechanism II (see Scheme 2), the polymers themselves could form residue such as SiO$_2$ or silicon-oxycarbide under the thermal degradation. Perhaps the degradation also followed mechanism II.

With respect to the degradation mechanisms of the samples containing VFS-oil, it was a little different from that of the SR. The mode of samples' decompositions could be changed with the incorporation of —CH$_2$CH$_2$CF$_3$.[41] In mechanism I, when one (or more) of the X$_1$, X$_2$, and X$_3$ represents the —CH$_2$CH$_2$CF$_3$, then it would be more difficult for the
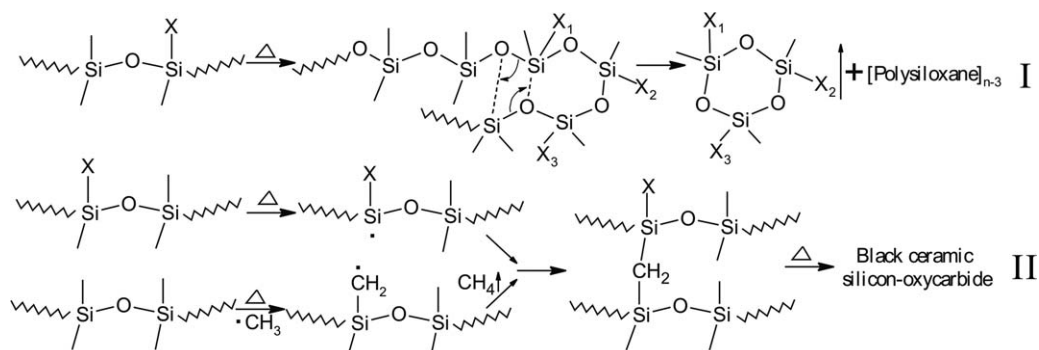
Scheme 2. Probable degradation mechanisms of the polysiloxane rubbers.

degradation mechanism I to take place due to steric hindrance caused by $-CH_2CH_2CF_3$. As reported,[43] when X_1, X_2, X_3 = $-CH_3$, the degradation activation energy of the mechanism I is about 43 kcal/mol, while it is 70 kcal/mol with regard to X_1, X_2, X_3 = $-CH_2CH_2CF_3$. Additionally, for the presence of $-CH_2CH_2CF_3$, the $-CH_3$ in the $-(CH_3)Si(CH_2CH_2CF_3)O-$ unit would be less stable and easier to be split into the methyl radicals at high temperature. Besides, thermal stability of $-CH_2CH_2CF_3$ is lower than $-CH_3$,[44] which could be used to illustrate the decline in the T_{10}. As the $-CH_3$ in the F unit were split into methyl radicals, the methyl in the adjacent chains would be attacked by the formed methyl radicals, which further helped to form methylene radical and methane as shown in mechanism II (see Scheme 2). Subsequently, the methylene bridged was formed, which was helpful to the formation of ceramic silicone-oxycarbide.[40] Since ceramic silicone-oxycarbide is much stable at high temperature, it contributed to the high residual mass of the samples. Thus, due to the presence of $-CH_2CH_2CF_3$, the decomposition of the FSRs was inclined to follow the mechanism II. Therefore, residual mass ratio increased (SR: 32.2%, FSR1/9: 45.8%, FSR2/8: 48.5%, FSR3/7: 51.4%, FSR4/6: 57.1) since the increasing VFS-oil content contributed to more ceramic silicon-oxycarbide within the degradation process. In sum, in spite of the slight decrease in thermal stability, it would not negatively affect the application of the RTV FSRs.

CONCLUSIONS

RTV FSRs with different dosages of VFS-oil were prepared in our experiments. The processability of the FSRs were evaluated by the rheological tests, and it was found that the available process condition could be obtained at relative higher

$$\dot{\gamma}$$

(>10 s^{-1}). The mechanical properties tests indicated that the VFS-oil did not exert any negative effect. The DMA results showed the reduction in samples' flexibility as the VFS-oil content increased. The crosslinking degree tests indicated that the crosslinking density was also not changed much as the VFS-oil increased, and this is consistent with the results of the mechanical properties test. The ASTM 1# oil immersion test showed that all samples exhibited the good resistance to ASTM 1# oil, and the resistance to the PDMS oil was well improved by addition of VFS-oil. The solvent resistance tests indicated that with the increasing VFS-oil content, the resistance to the acetone became worse but the resistance to the aliphatic solvents became better. ATR-FTIR spectra verified the presence of the $-CF_3$ group on the samples' surface. And the decrease in surface energy caused by $-CF_3$ was proved by the contact angle test. TGA showed that the thermal stability of the samples slightly decreased for the sake of VFS-oil. The residual mass ratio was increased as the $-CH_2CH_2CF_3$ content increased. This might be explained by the formation of ceramic silicone-oxycarbide and other stable residue, which is contributed by the increasing $-CH_2CH_2CF_3$ content.

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