Oil Resistance and Mechanical Properties of Polysiloxane Nanocomposites Prepared by *In Situ* Reaction of Reactive Polar Monomers

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ABSTRACT: A series of poly(methylvinylsiloxane) elastomer (VMQ) composites with improved oil resistance were prepared by introducing uniform polar polymer phases into VMQ matrix through the *in situ* reaction of reactive polar monomers—hydroxyethyl methacrylate (HEMA) and hydroxypropyl methacrylate (HPMA)—during peroxide curing. Differential scanning calorimetry and Fourier transform infrared measurements demonstrated that HEMA and HPMA had high reactivity and most of the monomers participated in the *in situ* reaction during peroxide curing. Transmission electron microscopic images showed that the uniform nanophases with the diameters in the range of 20–50 nm formed in the VMQ vulcanizates. The generated nanophases could interact with silica to form a strong filler network in the VMQ matrix, resulting in a significant increase of the modulus at low elongation of the VMQ vulcanizates. With increasing the content of polar monomers, the tensile strength decreased slightly, the elongation at break, the hardness and the 100% modulus increased, but the 300% modulus decreased significantly due to the decrease of the crosslink density. The incorporation of HEMA or HPMA into VMQ matrix could significantly improve the oil resistance of polysiloxane elastomer, and the oil resistance of the composites containing HEMA was a little better than that of the composites containing HPMA. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40983.

INTRODUCTION

Polysiloxane elastomers, with the structure $[—SiRR'—O—]_x$ exhibit a list of excellent properties including a large degree of flexibility, climate and oxidation resistance, thermal stability, low electrical conductivity, biocompatibility, low surface tension, and high permeability.[1,2] Due to these excellent properties, polysiloxane elastomers are widely used in aerospace industry, automobile industry, electronic industry, and biomedical applications.[2–6] However, most of polysiloxane elastomers have weak oil resistance, which seriously limit their practical application. Therefore, the production and consumption of polysiloxane elastomers would be significantly higher if the product could offer better resistance to oils.

Oil resistance, one of key characteristics in the final selection of the rubber to be used, is determined by the solubility parameters of elastomers and oils: the smaller the difference of solubility parameters is, the weaker the oil resistance of the elastomers is.[7]

Generally, the elastomers containing polar groups, such as nitrile rubber, epoxidized natural rubber, and fluororubber,[8–12] exhibit good oil resistance because most of the oils are nonpolar. Several approaches have been made to improve the oil resistance of silicone rubber. One of those approaches is introducing polar groups into silicone rubber chains by copolymerization to synthesize new polysiloxane elastomers, such as fluorosilicone elastomer[13–15] and cyanosilicone elastomer.[16] This approach needs complicated synthesis process and the price of these synthetic elastomers is often very high. Another approach is the blending polysiloxane elastomers with other polar elastomers, such as fluororubber[17,18] and acrylic rubber.[19] The property studies of fluororubber/silicone rubber blend carried by Ghosh et al. suggested that the blend has similar oil resistance to that of fluorosilicone rubber.[17] The problem of the blending method, however, is how to realize the good compatibility of different polymer phases, which is important for the properties of the blend. Dielectric properties measurements and dynamic mechanical thermal analyses reveal that the blends

Table I. The Formulation for Preparation of VMQ Composites

| Materials | Loading (phr[a]) | | | |
	VMQ/SiO$_2$	VMQ/SiO$_2$/HEMA (with different content of HEMA)	VMQ/SiO$_2$/HPMA (with different content of HEMA)	VMQ/SiO$_2$/HEMA (with different content of peroxide)
VMQ	100	100	100	100
Silica	40	40	40	40
hydroxyl silicone oil	2	2	2	2
HEMA	-	5/10/15/20	-	10
HPMA	-	-	5/10/15/20	-
TBPB	1	1	1	0.5/1.0/2.0/3.0

[a] phr is the abbreviation for weight parts per 100 g silicone rubber by weight.

of silicone rubber and fluororubber are thermodynamically immiscible.[20,21] To obtain a good compatibility of different polymer phases, a special compatibilizer has to be added during the mixing process. Guo et al.[22] used fluororubber grafted γ-methacryloxypropyltrimethoxysliane as a compatibilizer to prepare fluororubber/silicone rubber blends and found that the addition of the compatibilizer could improve the thermal stability, oil resistance, and mechanical properties. The third approach is the improving the oil resistance by adding some particles, such as ceria oxide,[23] but the improvement is very limited.

In recent years, the use of the radicals generated by peroxide during the curing of elastomers to initiate the reactive monomers to polymerize or be grafted on to elastomer chains has been proved to be an effective and convenient method to prepare elastomer composites with good dispersion and properties.[24–30] In this study, we attempted to improve the oil resistance of silicone rubber by introducing uniform polar polymer phases into silicone rubber matrix through the *in situ* reaction of some reactive polar monomers during peroxide curing. Two kind of monomers—hydroxyethyl methacrylate (HEMA) and hydroxypropyl methacrylate (HPMA)—were selected as reactive polar monomers to prepare silicone rubber composites. The morphology and properties studies showed that uniform nanophases were formed in silicone rubber matrix through *in situ* reaction method and the oil resistance of silicone rubber was significantly improved.

EXPERIMENTAL

Materials
Poly(methylvinylsiloxane) (VMQ) having 0.15% vinyl substituent and a molecular weight of 550,000 g mol^{-1} was obtained from Chenguang Chemical Research Institute, Sichuan, China. HPMA (purity 97%) and HEMA (purity 98%) were purchased form Aladdin, China. Silica (SiO$_2$, Degussa A200) with the diameter at about 12 nm was purchased from Degussa, German, and hydroxyl silicone oil was provided by Dow Corning, the United States. The peroxide used was tert-butyl peroxybenzoate (TBPB, purity 98%), which was purchased from Aladdin, China.

Preparation of Samples
VMQ, silica, and hydroxyl silicone oil were mixed by a 6-inch two-roll mill at room temperature for 20 min, and then HEMA

or HPMA monomers were added into the blend slowly. When all the monomers had been added, TBPB was added and mixed for 5 min. After mixing, the blends were cured at 145°C in an electrically heated hydraulic press (15 MPa) for their optimal cure time (t_{90}) determined by a curemeter. The formulation for preparation of VMQ composites is shown in Table I.

Measurements
Curing Characteristics of VMQ Blends. The curing characteristics of VMQ blends were determined with an oscillating disc rheometer (ODR, P3555B2) made by the Beijing Huanfeng Machinery Factory. The curing characteristics of the rubbers were characterized at 145°C, with an angular displacement of 3°, and a test frequency of 1.7 Hz.

Fourier Transform Infrared Spectroscopy (FTIR). FTIR analysis was performed on an FTIR spectrometer (Tensor 27, Bruker Optik Gmbh Co., Germany). The scan range was 4000–600 cm^{-1} with a resolution of 4 cm^{-1}.

Differential Scanning Calorimetry (DSC). DSC measurements were carried out on STARe system DSC1 instrument (Mettler-Toledo International Inc., Switzerland). The samples (5 ± 0.5 mg) were heated from 30°C to 200°C under nitrogen atmosphere at a heating rate of 10°C min^{-1}.

Transmission Electron Microscopy (TEM). Transmission electron microscopy (TEM) was carried out on an H-800-1 transmission electron microscope (Hitachi Co., Japan). The samples were cut by a microtome at −160°C and collected on cooper grids. The thickness of the samples for TEM measurement was about 100 nm.

Tensile Test. Tensile tests were performed on a CTM 4104 tensile tester (SANS, Shenzhen, China) at a cross-head speed of 500 mm min^{-1} and a temperature of 25°C ± 2°C according to GB/T 528–2009.

Oil Resistance Test. Oil resistance of VMQ vulcanizates was carried out according to GB/T 1690-92. The samples were immersed in ASTM 3# oils for 72 h at a given temperature. Then the samples were removed from the oil and wiped with tissue paper to remove the excess oil from the surface for oil resistance test. Oil resistance was reported in terms of changes
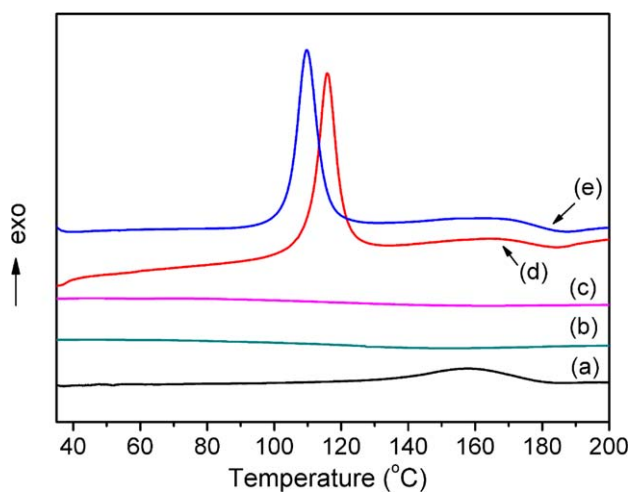
Figure 1. DSC curves of (**a**) VMQ/SiO$_2$ blend, (**b**) VMQ/SiO$_2$/HEMA blend without peroxide, (**c**) VMQ/SiO$_2$/HPMA blend without peroxide, (**d**) VMQ/SiO$_2$/HEMA blend with peroxide, and (**e**) VMQ/SiO$_2$/HPMA blend with peroxide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in volume and tensile properties after immersion. The volume of the sample can be measured by eq. (1):

$$V = \frac{m_1 g - m_2 g}{\rho g} = \frac{m_1 - m_2}{\rho} \qquad (1)$$

where m_1 and m_2 are the mass of the sample in the air and the mass of the sample in solvent, respectively, and ρ is the density of the solvent. The changes in the volume of the sample after immersed in ASTM 3# oils ($\triangle V$) can be calculated by eq. (2):

$$\Delta V = \frac{V' - V}{V} \times 100 \qquad (2)$$

where V and V' are the volume of the sample before and after immersed in ASTM 3# oils, respectively.

Rubber Processing Analysis. The storage moduli of the samples and their dependence on scanning strain were measured on a RPA2000 rubber processing analyzer (Alpha, the United States). Each sample ($\sim$5 g) was tested at 60°C, and the frequency used was 1 Hz.

Thermal Ageing of the Composites. The samples were placed in an oven at 200°C for 72 h. Then the samples were cooled at room temperature for 30 min, and the mechanical properties of the samples were measured by a CTM 4104 tensile tester (SANS, Shenzhen, China) at a cross-head speed of 500 mm min^{-1} and a temperature of 25°C $\pm$ 2°C according to GB/T 528-2009.

Compression set test (GB/T 7759-1996) was performed on the standard test sample of cylindrical shape of 29.0 $\pm$ 0.5 mm diameter and 12.5 $\pm$ 0.5 mm thickness vulcanized by compression molding method. The samples were compressed (the percentage of the compression was 25% of the original thickness) and placed in the oven at 200°C for 72 h. Then the samples were cooled at room temperature for 30 min and the thicknesses of the samples were measured. The compression set (C%) can be calculated by eq. (3):
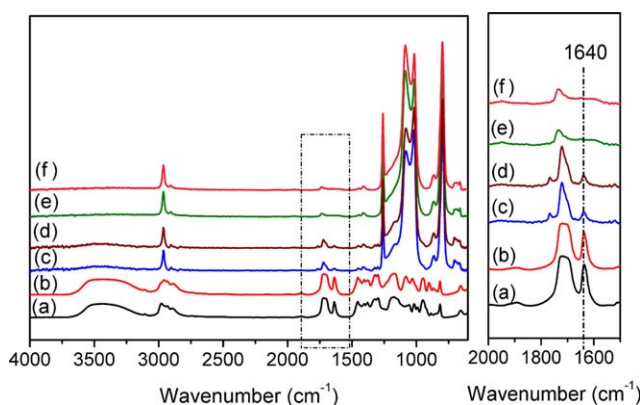
Figure 2. FTIR spectra of (**a**) HEMA, (**b**) HPMA, (**c**) VMQ/HEMA blend, (**d**) VMQ/HPMA blend, (**e**) VMQ/HEMA vulcanizate, and (**f**) VMQ/HPMA vulcanizate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$C\% = \frac{h_0 - h_2}{h_0 - h_1} \times 100\% \qquad (3)$$

where h_0, h_1, and h_2 were the original thickness of the sample, the thickness of the sample after compression ($h_1 = 9.3$ mm), and the thickness of the sample after thermal ageing, respectively.

Crosslink Density. The crosslink density of VMQ composites was determined by equilibrium swelling. A certain amount of samples (about 0.4 g) were swollen in toluene in a sealed vessel at 25°C $\pm$ 0.2°C for 3 days. Then the samples were taken out and immediately weighted on an analytical balance after the surface toluene was blotted off with tissue paper. Subsequently, the samples were dried in a vacuum oven at 80°C for 1 day to remove all the solvent and weighed again. The crosslink density of the sample (v_e) was calculated by Flory–Rehner equation:[31]

$$v_e = \frac{\rho_2}{M_e} = -\frac{\ln(1 - v_2) + v_2 + \chi v_2^2}{V_0(v_2^{1/3} - v_2/2)} \qquad (4)$$

where V_0 is the molar volume of the solvent (106.54 cm^3 mol^{-1} for toluene), ρ_2 is the density of gum VMQ vulcanizate, χ is the interaction parameter of VMQ and toluene and is taken as 0.465 here,[32] and v_2 is the volume fraction of the polymer in the vulcanizate swollen to equilibrium. The parameter v_2 was calculated by eq. (5):

$$v_2 = \frac{m_0 \phi(1 - \alpha)/\rho_2}{m_0 \phi(1 - \alpha)/\rho_2 + (m_1 - m_2)/\rho 1} \qquad (5)$$

where m_0, m_1, and m_2 are the masses of original sample, sample swollen to equilibrium, and dried sample, respectively, ϕ is the mass fraction of VMQ in the original sample, ρ_1 is the density of toluene, and α is the mass loss of gum VMQ vulcanizate during swelling.

RESULTS AND DISCUSSION

Evolution of *In Situ* Reaction of HEMA and HPMA

Figure 1 shows the DSC curves of VMQ/SiO$_2$ blend, VMQ/SiO$_2$/HEMA blends with and without peroxide, and VMQ/SiO$_2$/HPMA blends with and without peroxide. In the DSC
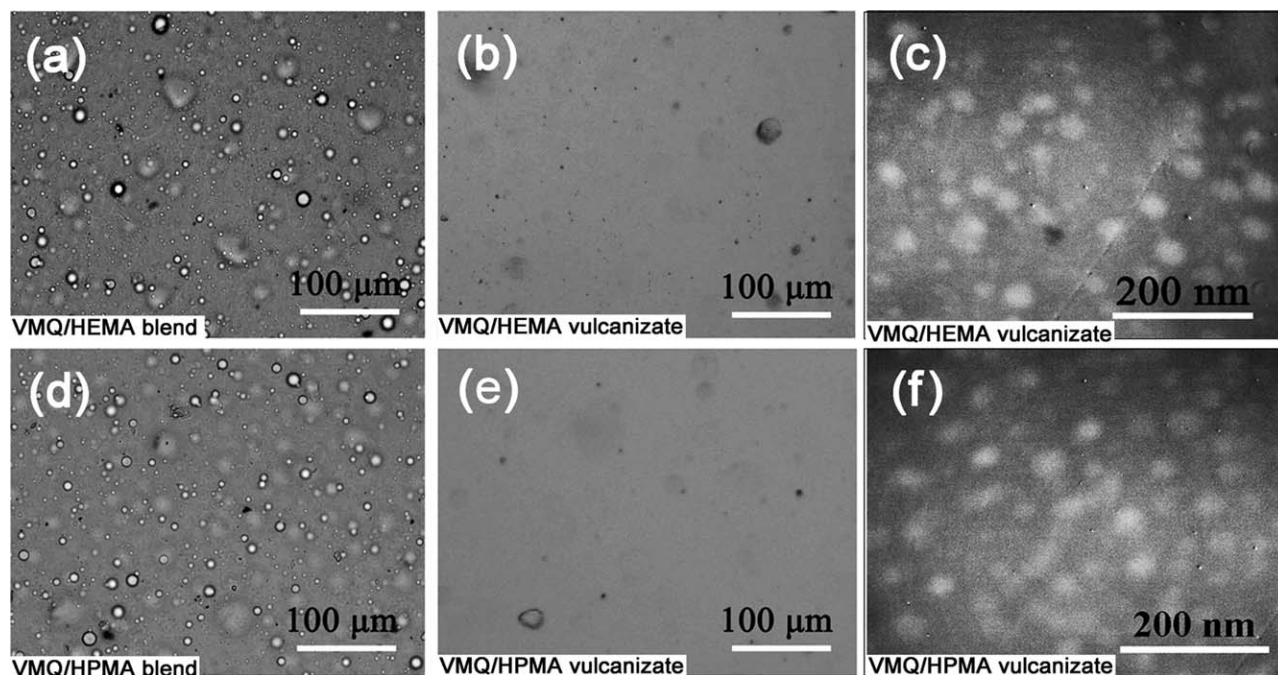
Figure 3. Optical micrographs of (**a**) VMQ/HEMA blend, (**b**) VMQ/HEMA vulcanizate, (**d**) VMQ/HPMA blend, and (**e**) VMQ/HPMA vulcanizate; TEM images of (**c**) VMQ/HEMA vulcanizate and (**f**) VMQ/HPMA vulcanizate.

curve of VMQ/SiO$_2$ blend [Figure 1(a)], there is a broad exothermic peak ranging from 130°C to 180°C; the exothermic peak probably corresponds to the crosslinking of silicone rubber. For the blends without peroxide [Figure 1(b,c)], none of peaks can be seen in DSC curves, illustrating that HEMA and HPMA monomers are relatively stable in VMQ matrix without peroxide. However, strong sharp exothermic peaks can be seen in the DSC curves of the blends containing peroxide: the exothermic peak of VMQ/SiO$_2$/HEMA blend appears at about 116°C, and the exothermic peak of VMQ/SiO$_2$/HPMA blend appears at about 110°C. Those sharp peaks are probably due to the *in situ* reaction of HEMA or HPMA monomers initiated by the radicals generated from the decomposition of peroxide at that temperature. Besides the sharp exothermic peaks, a board exothermic peak ranging from 130°C to 180°C can

also be seen in the DSC curves of VMQ/SiO$_2$/HEMA blend and that of VMQ/SiO$_2$/HPMA blend.

It can be concluded from the DSC curves that both HEMA and HPMA have high reactivity in silicone rubber matrix. In this study, FTIR was further performed to verify the *in situ* reaction of HEMA and HPMA in VMQ matrix during the peroxide curing. Figure 2 shows FTIR spectra of HEMA, HPMA, VMQ/HEMA blend, VMQ/HPMA blend, VMQ/HEMA vulcanizate, and VMQ/HPMA vulcanizate. The bands at 1640 cm^{-1} in Figure 2(a,b) are assigned to the C=C stretching vibration of HEMA and HPMA, respectively. In VMQ/HEMA blend [Figure 2(c)] and VMQ/HPMA blend [Figure 2(d)], the two sharp bands at 1015 and 1087 cm^{-1} are attributed to the stretching vibration of Si—O—Si, and the sharp band at 796 cm^{-1} is attributed to the stretching vibration of Si—C. The C=C
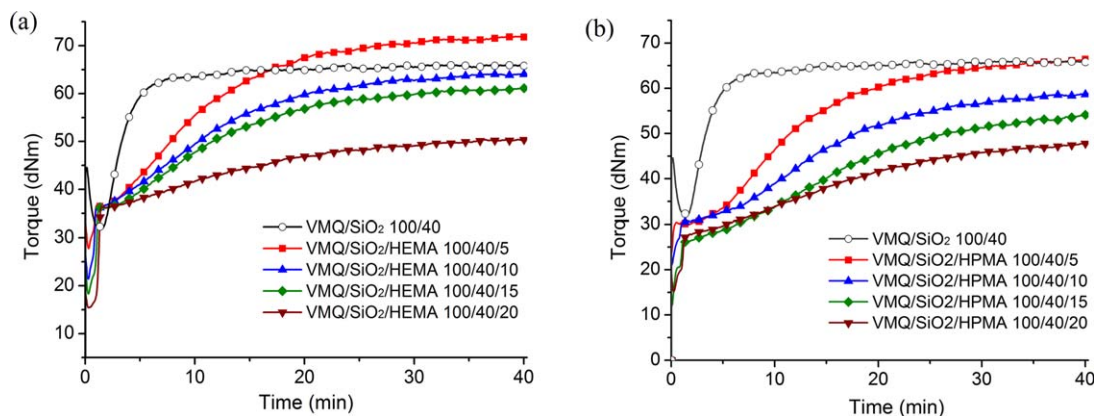
Figure 4. The characteristics of VMQ/SiO$_2$ blend, VMQ/SiO$_2$/HEMA blends, and VMQ/SiO$_2$/HPMA blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
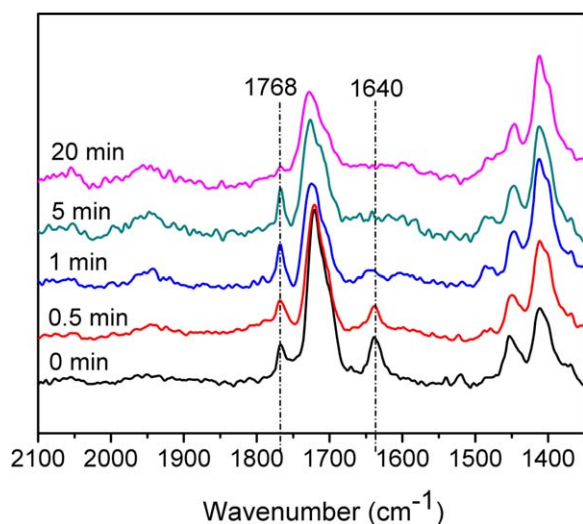
Figure 5. FTIR spectra of VMQ/SiO₂/HEMA blend cured for different set time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

characteristics of HEMA or HPMA can be still seen in the blends, although the intensity of the peaks decreases as a result of the concentration effect. However, the band at 1640 cm^{-1} disappear in the FTIR spectra of VMQ/HEMA vulcanizate and VMQ/HPMA vulcanizate, illustrating that most of HEMA or HPMA monomers have participated the *in situ* reaction in VMQ matrix during peroxide curing.

Morphology Analysis
The morphology of the samples containing HEMA or HPMA was studied by polarizing optical microscope and TEM. In the VMQ/HEMA blend [Figure 3(a)] and the VMQ/HPMA blend [Figure 3(d)], HEMA, or HPMA monomers exist in the form of liquid drops with the diameter in the range of 0–20 μm. During the curing, these monomers polymerize to *poly*-HEMA or *poly*-HPMA initiated by the radicals generated from peroxide. However, only several particles corresponding to *poly*-HEMA or *poly*-HPMA can be seen in the VMQ/HEMA vulcanizate [Figure 3(b)] and the VMQ/HPMA vulcanizate [Figure

3(e)], illustrating that the generated particles are well dispersed in VMQ matrix. TEM was performed to further study the dispersion of these generated particles in the vulcanizates. In the VMQ/HEMA vulcanizate [Figure 3(b)] and VMQ/HPMA vulcanizate [Figure 3(e)], the dark phase presents VMQ matrix because silicone rubber has a higher electron density than *poly*-HEMA or *poly*-HPMA does. It can be seen form TEM images that the generated particles by the *in situ* reaction of HEMA or HPMA are well dispersed in VMQ matrix and the size of these particles is in the range of 20–50 nm. The dispersion of *poly*-HPMA particles is a little better than that of *poly*-HEMA particles probably because HPMA has low polarity and better solubility in VMQ matrix than HEMA does. In addition, the boundary of the generated nanoparticles is not clear, implying a good compatibility between these nanoparticles and silicone rubber. Considering the difference in the polarity of silicone rubber and these generated nanoparticles, we could ascribe the good compatibility to the formation of chemical bonds between these nanoparticles and silicone rubber at the presence of the peroxide.

Curing Characteristics
In this study, we firstly prepared VMQ/SiO₂/HEMA or VMQ/SiO₂/HPMA composites with different content of HEMA or HPMA, and investigated the properties of these composites. All the composites were cured by 1 phr TBPB. Figure 4 shows the curing curves of VMQ/SiO₂ blend, VMQ/SiO₂/HEMA blends and VMQ/SiO₂/HPMA blends. It can be seen that the curing curve of VMQ blend containing HEMA or HPMA is quite different from that of VMQ/SiO₂ blend. For the VMQ/SiO₂ blend, it shows two stages in the curing curve: the decrease of torque at very beginning of curing is caused by the decrease in viscosity as the temperature increases from room temperature to curing temperature; the subsequent increase of torque is attributed to the crosslinking of silicone rubber. For the VMQ/SiO₂/HEMA blends and the VMQ/SiO₂/HPMA blends, however, they show another stage—a significant increase of torque—before the crosslinking of silicone rubber. The significant increase of torque is probably due to the *in situ* reaction of HEMA or HPMA monomers. In the blend, HEMA or HPMA monomers exist in the form of liquid drops, and these liquid drops can act as

Table II. Mechanical Properties of VMQ/SiO₂ Vulcanizate, VMQ/SiO₂/HEMA Vulcanizates, and VMQ/SiO₂/HPMA Vulcanizates

| Samples	100% modulus (MPa)	300% modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Shore A hardness (°)	Permanent set (100%)
VMQ/SiO₂ (100/40)	1.42	6.24	9.43	394	58	0
VMQ/SiO2/HEMA (100/40/5)	1.75	6.02	8.25	383	63	8
VMQ/SiO2/HEMA (100/40/10)	1.77	5.24	7.81	393	70	10
VMQ/SiO2/HEMA (100/40/15)	1.98	4.81	7.47	416	75	12
VMQ/SiO2/HEMA (100/40/20)	2.23	4.38	5.09	349	80	20
VMQ/SiO2/HPMA (100/40/5)	1.50	5.47	9.44	426	63	12
VMQ/SiO2/HPMA (100/40/10)	1.56	3.93	9.28	527	68	16
VMQ/SiO2/HPMA (100/40/15)	1.57	3.88	8.72	510	72	20
VMQ/SiO2/HPMA (100/40/20)	1.96	3.37	7.48	607	75	28
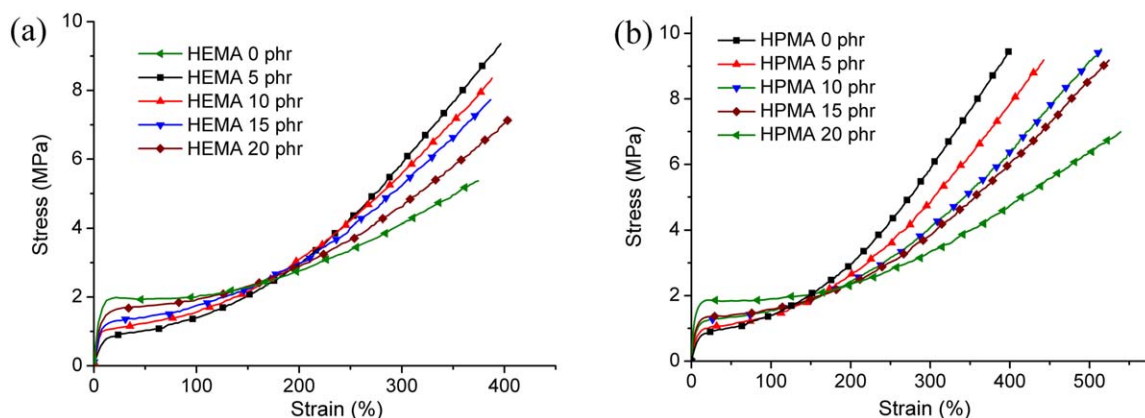
Figure 6. The stress–strain curves of VMQ/SiO$_2$ vulcanizate, (**a**) VMQ/SiO$_2$/HEMA vulcanizates, and (**b**) VMQ/SiO$_2$/HPMA vulcanizates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

plasticizers which would reduce the viscosity of blends at the beginning of curing. When these monomers polymerize to *poly-*HEMA or *poly-*HPMA in VMQ matrix, the liquid drops transform to particles and the viscosity of blends increases significantly. The result from the curing curves demonstrates that the HEMA and HPMA monomers have high reactivity and the *in situ* reaction will complete at beginning of peroxide curing.

FTIR was performed to study the degree of reaction with curing time by investigate the intensity of the band for C═C stretching vibration. Figure 5 shows FTIR spectra of VMQ/SiO$_2$/HEMA blend with different curing time. The FTIR spectra of all the samples cured for different curing times were normalized by band at 1087 cm^{-1} for Si─O─Si stretching vibration (shown in Figure 2) because the intensity of this band is nearly unchanged during peroxide curing. It can be clearly seen from Figure 5 that the intensity
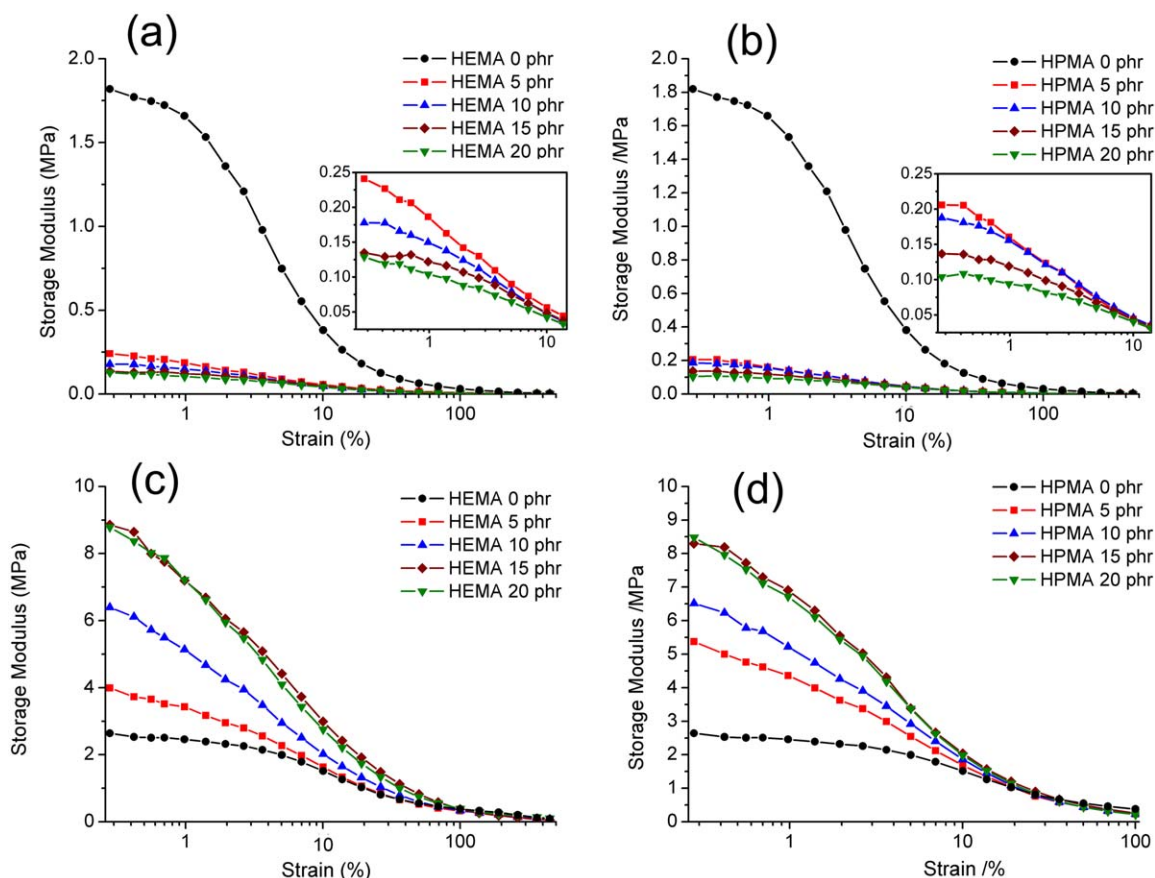
Figure 7. The relation between the storage modulus and strain of (**a**) VMQ/SiO$_2$/HEMA blends, (**b**) VMQ/SiO$_2$/HPMA blends, (**c**) VMQ/SiO$_2$/HEMA vulcanizates, and (**d**) VMQ/SiO$_2$/HPMA vulcanizates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
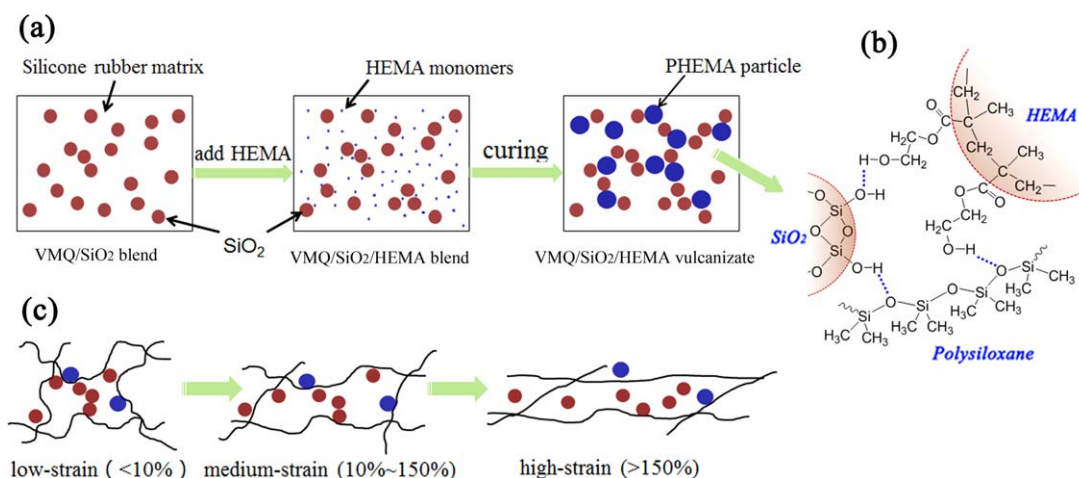
Figure 8. Scheme of the filler network and the interaction among SiO_2, HEMA particles, and polysiloxane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the band at 1640 cm^{-1} for C=C stretching vibration decreases obviously during the curing. The most obvious decrease of the intensity of 1640 cm^{-1} band occurs at the curing time less than 1 min, indicating the significant *in situ* reactions of HEMA take place during that time. The FTIR result is consistent with that from curing curves in Figure 4. Besides, the band for C=C stretching vibration completely disappears when the curing time reaches 1 min, illustrating that all the HEMA monomers have participated in the *in situ* reaction. The band at 1768 cm^{-1} is attributed to the stretching vibration of C=O in the peroxide TBPB. In the FTIR spectrum of the VMQ/SiO$_2$/HEMA blend cured for 1 min, the stretching vibration of C=O can be seen clearly, illustrating only a few peroxide has been decomposed. The FTIR spectra demonstrate that the *in situ* reaction (mainly polymerization of HEMA) can occur in the presence of a few radicals.

In addition, the incorporation of HEMA or HPMA into silicone rubber matrix can affect the curing time of the VMQ blends and the torque of the final VMQ composites (see Figure 4). As the contents of HEMA or HPMA increase, the curing time increases and the maximum torque decreases significantly. The increase of the curing time and the decrease of the maximum

torque could be ascribed to the *in situ* reaction of HEMA or HPMA with the peroxide. On the one hand, the radicals generated from the peroxide can initiate the polymerization of HEMA or HPMA. On the other hand, the radicals can reacted with the —CH$_3$ or —CH$_2$ in the PHEMA or PHPMA to form the polymer radicals, which can further react with other polymer radicals (PHEMA/PHPMA radicals and polysiloxane radicals) to form crosslinked PHEMA (or crosslinked PHPMA) and PHEMA-graft-polysiloxane (or PHPMA-graft-polysiloxane). Because of the consumption of the peroxide by HEMA or HPMA, only part of curing agents participate in the crosslinking of the silicone rubber, leading to the decrease in maximum torque and the increase in curing time. Based on the FTIR spectra and curing curves, it can be concluded that the polymerization of HEMA or HPMA mainly occurs at the beginning of curing (<1 min), and then the crosslink reactions and grafting reactions occurs.

Mechanical Properties

Table II shows the mechanical properties of VMQ/SiO$_2$ vulcanizate, VMQ/SiO$_2$/HEMA vulcanizate, and VMQ/SiO$_2$/HPMA vulcanizate. For VMQ/SiO$_2$/HEMA vulcanizates, with increasing the content of HEMA, the tensile strength decreases while the hardness and the permanent set increase. Compared with that of VMQ/SiO$_2$ vulcanizate, the elongation at break of VMQ/SiO$_2$/HEMA vulcanizates does not change much. For VMQ/SiO$_2$/HPMA vulcanizates, the tensile strength, hardness, and permanent set show the similar trend as those of VMQ/SiO$_2$/HEMA vulcanizates with increasing the content of HPMA; at the same content of monomers; however, the VMQ/SiO$_2$/HPMA vulcanizates show higher tensile strength than VMQ/SiO$_2$/HPMA vulcanizates does probably because of the dispersion of HPAM is better than that of HEMA. The elongation at break of VMQ/SiO$_2$/HPMA vulcanizates increases significantly with increasing the content of HPMA. For example, the elongation at break of the VMQ/SiO$_2$/HPMA vulcanizate containing 20 phr HPMA is higher than 600%. In addition, for both VMQ/SiO$_2$/HEMA vulcanizates and VMQ/SiO$_2$/HPMA vulcanizates, the 100% modulus increases with increasing the content

Table III. The Parameters of the Swelling Equilibrium Measurement of the Samples

Sample	v_2 (%)	M_c (g mol^{-1})	v_e (10^{-4} mol cm^{-3})
VMQ/SiO$_2$ (100/40)	0.271	4826	2.01
VMQ/SiO$_2$/HEMA (100/40/5)	0.226	7951	1.22
VMQ/SiO$_2$/HEMA (100/40/10)	0.217	8899	1.09
VMQ/SiO$_2$/HEMA (100/40/15)	0.214	9238	1.05
VMQ/SiO$_2$/HEMA (100/40/20)	0.212	9510	1.02
VMQ/SiO$_2$/HPMA (100/40/5)	0.213	9326	1.04
VMQ/SiO$_2$/HPMA (100/40/10)	0.201	10899	0.89
VMQ/SiO$_2$/HPMA (100/40/15)	0.195	11829	0.82
VMQ/SiO$_2$/HPMA (100/40/20)	0.182	14058	0.69
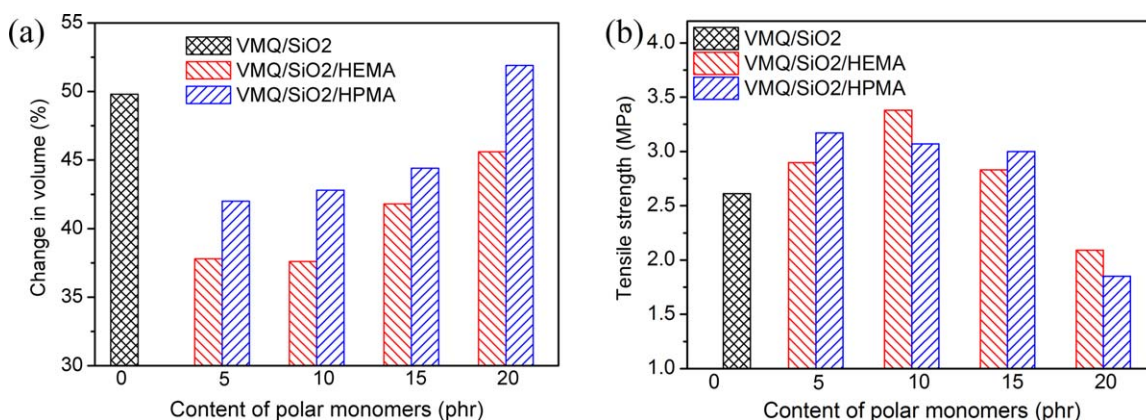
Figure 9. The oil resistance of different vulcanizates: (**a**) the change in volume of the vulcanizates and (**b**) the tensile strength of the vulcanizates after oil immersion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of HEMA or HPMA monomers, but the 300% modulus decreases as the content of HEMA or HPMA monomers increases. The different change trend of the 100% modulus from that of 300% modulus implies that HEMA or HPMA has different effect on the stress at low elongation and that at high elongation. As can be seen form the stress-strain curves of the vulcanizates in Figure 6, the vulcanizate containing higher content of HEMA or HPMA shows higher stress at the elongation below 150% but lower stress at the elongation over 200%. For the vulcanizates containing high content of HEMA or HPMA, the stress increases significantly at the low elongation (<10%) but then does not change much at the elongation between 10% and 150%. The sharp increase of stress at the low elongation and the subsequent plateau are probably attributed to the formation of filler network and the slippage of silicone rubber chains on the nanoparticles, respectively.

The effect of the amplitude-dependence of the dynamic viscoelastic properties of filled rubbers is often referred to as the Payne effect,[33] which reflects disruption–formation process of the filler network produced by the interaction of the filler-filler and filler-rubber in the compound.[34] The dependency of the storage modulus (G') as a function of strain for different blends and vulcanizates are shown in Figure 7. As can be seen form the storage modulus-strain curves in Figure 7(a,b), the storage modulus decreases significantly when a small content of HEMA or HPMA monomers are incorporated into the blend, and then decreases slightly with increasing the content of monomers. The decrease of storage modulus implies a decrease of silica-silica interaction. For the vulcanizates [Figure 7(c,d)], however, the storage modulus increases significantly with increasing the content of HEMA or HPMA monomers, implying that a strong network is formed in the VMQ matrix after curing.

Based on the results from FTIR analysis, TEM images and the storage modulus-strain curves, the filler network and the interaction among SiO$_2$, HEMA particles and polysiloxane can be demonstrated in Figure 8(a,b), respectively. The HEMA or HPMA monomers contain hydroxyl groups, which can interact with the hydroxyl groups on the surface of silica. The addition of HEMA or HPMA monomers into VMQ/SiO$_2$ blends can decrease the silica–silica interaction, leading to a decrease of the

storage modulus. In the vulcanizates, HEMA or HPMA monomers have participated in the *in situ* reaction and formed rigid nanoparticles with the size in the range of 20–50 nm. These generated nanoparticles interact with silica [Figure 8(b)] and formed a strong filler network in the vulcanizates [Figure 8(a)], resulting in a significant increase of the storage modulus. In addition, the silica and the generated HEMA or HPMA nanoparticles process a certain extent of ability to adsorb silicone rubber chains onto their surface through physical adsorption, as shown in Figure 8(b). Except for the physical adsorption, chemical links between the generated HEMA or HPMA nanoparticles and silicone rubber chains are also supposed to exist in the vulcanizates after peroxide curing.

Figure 8(c) shows the change of filler network in the vulcanizates during the stretching. At low strain (<10%), the filler network cannot be destroyed and has a major contribution for the modulus of the vulcanizates.[35] As the content of HEMA or HPMA increases, the filler network becomes stronger and the vulcanizate shows higher modulus. When the strain is higher than 10%, the filler network is destroyed and the silicone rubber chains begin to slip on the surface of fillers to form stretching or parallel-arraying chains.[36] Hence, the stress does not increase much in the strain between 10% and 150% during stretching. At high strain (>150%), more and more silicone rubber chains are stretched and the rubber chains with high orientation will share the stress together,[36] so the stress begins to increase significantly.

The crosslink density can influence the slippage of silicone rubber chains on the filler surface and affect the mechanical properties.[33] Considering the HEMA or HPMA monomers consume a part of peroxide to participate the *in situ* reaction during the curing, we can ascribe that the vulcanizate containing high content of HEMA or HPMA monomers shows low stress at high elongation to the decrease of crosslink density. The average molecular weight (M_c) between the crosslinking points and the cross-linking density (ν_e) are listed in Table III. As shown in Table III, the crosslink density decreases significantly when a small content of HEMA or HPMA monomers are added into silicone rubber matrix, and then decreases slightly with

increasing the content of HEMA or HPMA monomers. In addition, the VMQ/SiO$_2$/HPMA vulcanizate has a lower crosslink density than VMQ/SiO$_2$/HEMA vulcanizate does at the same content of monomers, probably because the dispersion of HPMA monomers is better than that of HEMA monomers and more peroxide is consumed by HPMA monomers than that by HEMA monomers.

Oil Resistance

The results of oil resistance based on the changes in volume and in tensile strength are shown in Figure 9. As shown in Figure 9(a), the change in volume of VMQ vulcanizates decreases significantly when a small content of polar monomers are added into silicone rubber matrix. For example, the volume change of VMQ/SiO$_2$ vulcanizate is about 50%, but that of the VMQ/SiO$_2$/HEMA vulcanizate containing 10 phr HEMA decreases to 37.2%. Meanwhile, the vulcanizates containing HEMA or HPMA monomers shows higher tensile strength than the VMQ/SiO$_2$ vulcanizate does after oil immersion, as shown in Figure 9(b). For example, the tensile strength of VMQ/SiO$_2$ vulcanizate is 2.57 MPa, but the VMQ/SiO$_2$/HEMA vulcanizate containing 10 phr HEMA increases to 3.48 MPa. The results from Figure 9 demonstrate that the addition of polar nanoparticles by *in situ* reaction method can improve the oil resistance of silicone rubber. Two reasons can attribute to the improvement of oil resistance: the increase of polarity and the formation of strong filler network. During peroxide curing, some HEMA monomers are supposed to be grafted onto silicone rubber chain, resulting in an increase of polarity and improvement of oil resistance. On the other hand, there is a strong interaction between HEMA or HPMA particles, SiO$_2$ and silicone rubber chains, as shown in Figure 8(b). The strong interaction can prevent the oil molecules to permeate into the vulcanizate, leading to an improvement of oil resistance. In addition, it can be seen from Figure 9(b) that the change in volume of the vulcanizates containing HPMA is higher than that of the vulcanizates containing HEMA, probably because HEMA has higher polarity than HPMA does and the VMQ/SiO$_2$/HEMA vulcanizates have higher crosslink density than the VMQ/SiO$_2$/HPMA vulcanizates do. With increasing the content of polar monomers, the change in volume of the vulcanizate after oil immersion decreases first and then increases at high content of polar monomers, while the tensile strength increases first and then decrease at high content of polar monomers. The vulcanizates show best oil resistance when the content of polar monomers ranges from 5 to 10 phr.

The VMQ/SiO$_2$/HEMA vulcanizates containing 5 phr HEMA and 10 phr HEMA were selected to further study the oil resistance of VMQ/SiO$_2$/HEMA vulcanizates at different temperature. Table IV shows the oil resistance of VMQ/SiO$_2$ vulcanizates and VMQ/SiO$_2$/HEMA vulcanizates at different temperature. As the temperature increases, the volume change increases significantly, and the tensile strength and hardness decrease dramatically. Compared with the VMQ/SiO$_2$ vulcanizates, the vulcanizates containing HEMA show less change in the volume change, tensile strength and the hardness as the temperature increases, illustrating that the addition of HEMA could improve the oil resistance of VMQ. The mechanical properties of VMQ vulcanizates after thermal ageing (200°C × 72 h) were also studied in

Table IV. The Oil Resistance of the Composites at Different Temperature and the Mechanical Properties of the Composites After Thermal Ageing

Sample	VMQ/ SiO$_2$ (100/40)	VMQ/ SiO$_2$/ HEMA (100/ 40/5)	VMQ/ SiO$_2$/ HEMA (100/ 40/10)
Oil resistance (ASTM 3# oil)			
25°C × 70 h			
Volume change, %	+17.3	+15.3	+15.1
Change in shore A hardness, °	−14	−12	−9
Tensile strength, MPa	6.10	5.75	6.62
Elongation at break, %	262	234	270
100°C × 70 h			
Volume change, %	+31.3	+27.4	+27.2
Change in shore A hardness, °	−24	−20	−18
Tensile strength, MPa	4.32	4.77	5.12
Elongation at break, %	213	188	232
125°C × 70 h			
Volume change, %	+40.2	+33.5	+32.7
Change in shore A hardness, °	−33	−26	−24
Tensile strength, MPa	3.22	4.05	4.08
Elongation at break, %	230	215	210
150°C × 70 h			
Volume change, %	+49.8	+37.8	+37.3
Change in shore A hardness, °	−38	−30	−28
Tensile strength, MPa	2.57	2.92	3.48
Elongation at break, %	292	245	223
175°C × 70 h			
Volume change, %	+62.0	+48.8	+46.4
Change in shore A hardness, °	−44	−36	−31
Tensile strength, MPa	1.98	2.48	3.26
Elongation at break, %	310	330	296
Thermal ageing (200°C × 70 h)			
Shore A hardness, °	72	76	78
100% modulus, MPa	3.56	4.73	5.75
Tensile strength, MPa	7.13	6.43	6.45
Elongation at break, %	190	156	130
Compression set, %	88.2	89.3	89.4

this study, as shown in Table IV. After thermal ageing, the tensile strength decreased slightly, but the 100% modulus and the hardness increased significantly. The elongation at break also decreased dramatically after thermal ageing. The increase of the 100% modulus and the decrease of the elongation at break could be ascribed to the increase of the crosslink density during the thermal ageing process. In addition, all the vulcanizates show very high compression set. On the one hand, during the thermal ageing, some crosslinks were probably broken, so when the load was removed the sample could not recover to its original thickness.[37] On the other hand, new crosslinks, as mentioned above, were probably formed during the compression of

Table V. The Mechanical Properties and Crosslink Density of VMQ/SiO$_2$/HEMA (100/40/10) Vulcanizates Cured by Different Content of Peroxide

Samples	100% modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Shore A hardness (°)	Permanent set (100%)	Crosslink density, (10^{-4} mol cm^{-3})
TBPB 0.5 phr	1.51	2.83	336	68	32	0.58
TBPB 1 phr	1.77	7.81	393	70	10	1.08
TBPB 2 phr	2.53	6.98	258	72	6	1.62
TBPB 3 phr	2.91	5.76	200	73	4	1.83

the samples. These new crosslinks could resist the recovery of the sample when the load was removed, resulting in an high compression set. The results of the compression set implying that these VMQ vulcanizates show weak properties at the temperature higher than 200°C.

As illustrated in Table III, the crosslink density of VMQ vulcanizates decreases when a small content of HEMA or HPMA monomers are added into VMQ matrix; the decrease of crosslink density may affect the oil resistance. To study the effect of the polar monomers on the oil resistance of VMQ vulcanizates, VMQ/SiO$_2$/HEMA (100/40/10) vulcanizates with different content of peroxide was prepared for oil resistance test. Table V shows the mechanical properties and crosslink density of VMQ/SiO$_2$/HEMA vulcanizates cured by different content of peroxide. With increasing the content of peroxide, the 100% modulus and shore A hardness increase, the permanent set decrease, and the tensile strength and elongation at break increases first but then decreases when the content of peroxide is higher than 1 phr. The crosslink density also increases as the content of TBPB increases, and the crosslink density of the VMQ/SiO$_2$/HEMA vulcanizates cured by 3 phr TBPB is similar to that of VMQ/SiO$_2$ vulcanizate (1.90 × 10^{-4} mol cm^{-3}). Figure 10 shows the change in volume and tensile strength of VMQ/SiO$_2$/HEMA vulcanizates cured by different content of peroxide after oil immersion. As the crosslink density increases, the change in volume of VMQ/SiO$_2$/HEMA vulcanizates decreases and the tensile

strength after oil immersion increases. When the crosslink density is similar, the VMQ/SiO$_2$/HEMA vulcanizate show better oil resistance than VMQ/SiO$_2$ vulcanizate does. The change in volume and tensile strength of VMQ/SiO$_2$/HEMA vulcanizate cured by 3 phr TBPB after oil immersion are 35% and 3.8 MPa, but those of VMQ/SiO$_2$ vulcanizate after oil immersion are 50% and 2.6 MPa, illustrating that the addition of HEMA into VMQ matrix can greatly improve the oil resistance.
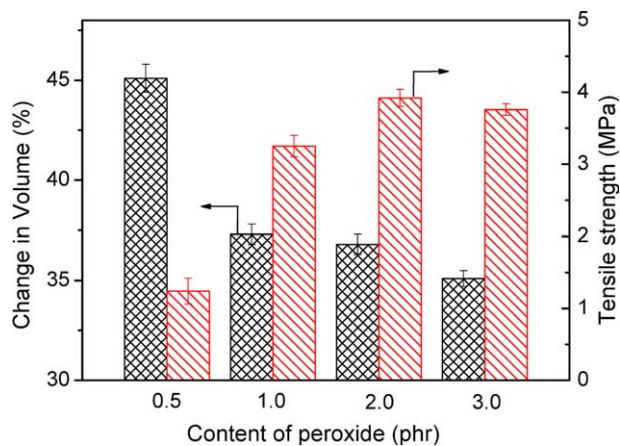
CONCLUSIONS

In this study, HEMA and HPMA were selected as reactive polar monomers to incorporate into VMQ matrix and prepared VMQ composites by *in situ* reaction method. HEMA and HPMA shows high reactivity and most of the monomers can participate into the *in situ* reaction to form uniform nanophases with the diameters in the range of 20–50 nm in VMQ matrix. The generated nanophases contain a lot of hydroxyl groups and these hydroxyl groups could interact with those on the surface of silica to form a strong filler network in VMQ matrix. HEMA and HPMA have a great influence on the mechanical properties and crosslinking structure of VMQ composite. With increasing the content of polar monomers, the tensile strength decreases slightly, the elongation at break, the hardness and the 100% modulus increase, and the 300% modulus and crosslink density decrease significantly. The oil resistance of VMQ composites can be greatly improved when a small content of HEMA or HPMA are incorporation into VMQ matrix. At the same content of reactive polar monomers, the composites containing HEMA show better oil resistance than those containing HPMA do.

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Figure 10. Change in volume and tensile strength of VMQ/SiO$_2$/HEMA (100/40/10) vulcanizates cured by different content of peroxide after oil immersion. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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