EFFECT OF THE CHEMICAL NATURE OF MQ COPOLYMERS ON THE RHEOLOGICAL PROPERTIES OF COMPOSITIONS ON THEIR BASIS

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Abstract

The rheological and rheokinetic properties of the compositions based on low-molecular rubber polyisoprene and MQ copolymer particles with decyl terminal groups were studied. The effect of the ratio of M and Q units in the copolymer on the rheological and mechanical properties of the compositions was analyzed. An increase in the length of a hydrocarbon substituent in M units was shown to lead to an increase in the affinity of the copolymer to the carbon-chain polymer matrix. An increase in the content of Q units facilitates the growth of the elastic modulus of the cured composites.
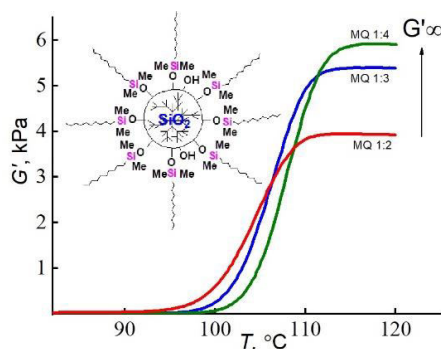
Key words: MQ copolymer, rheological properties, elastic modulus.

Introduction

The development of chemistry of silica fillers is intrinsically connected with the synthesis of new siloxane nanogels: MQ copolymers, molecular silica sols, polyorganosilsesquioxanes, and other organosilicon products. Of particular interest in recent years are MQ copolymers [1, 2]. These objects are considered not only as functional additives, but also as promising reinforcing agents [3]. MQ copolymers combine the properties of inorganic particles and organic compounds, which is stipulated by the presence of a silica (SiO_2) core and an organic shell, the nature of which can be varied. The possibility of controlling the functional groups allows one to combine an inorganic filler with polymer matrices of various chemical compositions. These molecular objects exhibit very high compatibility with both carbon-chain and silicone rubbers [4, 5].

Most of the reports are devoted to MQ copolymers with methyl terminal groups. The practical application of these compounds is mainly associated with the modification of polymer compositions based on organosilicon compounds [6, 7]. Such copolymers are considered as modifying additives that improve the thermal resistance of materials, adhesion enhancing agents for silicone adhesives, and plasticizers [8–10]. The main advantage of MQ copolymers is their high compatibility with silicone polymers.

The substitution of methyl groups in MQ copolymers for other organic moieties opens up new prospects and expands their application scope. Thus, vinyl- and phenyl-substituted MQ copolymers were proposed as the additives for thermally resistant and optically transparent coatings based on a silicone rubber [11, 12]. Chen *et al.* [13] suggested ureido-modified MQ resins as an additive to an insulating material in order to increase its resistance to erosion. A number of works showed the possibility of using the resins with vinyl and methoxy groups as cross-linking agents for silicone rubbers [14, 15].

Our recent studies showed that the use of siloxane nanogels of different compositions in rubber-based compositions makes it possible to consider them as molecular fillers and to effectively control the properties of such compositions [16–18, 3, 4, 7].

In this work, the main focus was on the synthesis of MQ copolymers bearing decyl groups in M units, at different ratios of M and Q units. The possibility of using such siloxane nanogels as a reinforcing filler for the compositions based on carbon-chain rubbers has been studied. One of the key issues in the application of MQ copolymers as fillers is the assessment of their effect on the rheological properties of the resulting compositions as well as on the mechanical properties of the cured systems.

Results and discussion

Synthesis

A series of decyl-containing MQ resins consisting of $DecMe_2SiO_{1/2}$ (M) and $SiO_{4/2}$ (Q) units with the M/Q molar ratios equal to 1:2, 1:3, and 1:4 were used as nanogel fillers. They were obtained by the polycondensation of 1,3-didecyl-1,1,3,3-tetramethyldisiloxane (M) and tetraethoxysilane (Q) in glacial acetic acid according to Scheme 1.

At the M/Q ratio of 1:2, the synthesis was performed by the earlier described method [19], using an excess of acetic acid and acetyl chloride as a catalyst at 125 °C. When the content of Q units was increased to 1:3 and 1:4 ratios, these conditions lead to the formation of a cross-linked insoluble product. Therefore, in these cases the reactions were performed under milder conditions, reducing the temperature to 80 °C, avoiding an excess of acetic acid, and using the ratio of acetic acid to the
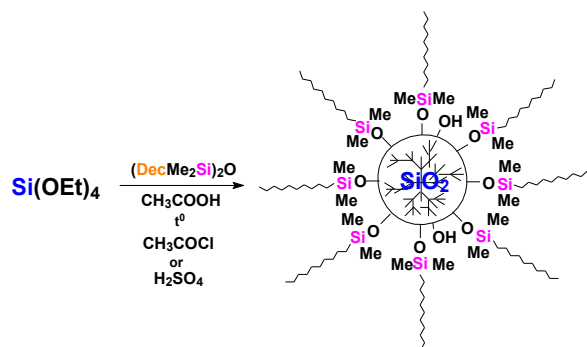
Scheme 1. Synthesis of decyl-containing MQ resins.

Figure 2. ^{1}H NMR spectrum of the MQ resin with 1:4 ratio of the units blocked with chloro(dimethyl)vinylsilane.

alkoxy groups of tetraethoxysilane equal to 1:1. Sulfuric acid was used as a catalyst. The reaction completion was determined by the disappearance of the alkoxy group signals in the ^{1}H NMR spectra. Figure 1 shows an example of such a spectrum of the reaction product for the M/Q ratio of 1:3.

As a result, a series of MQ resins were obtained that were stable at all M/Q ratios in solutions of polar organic solvents.
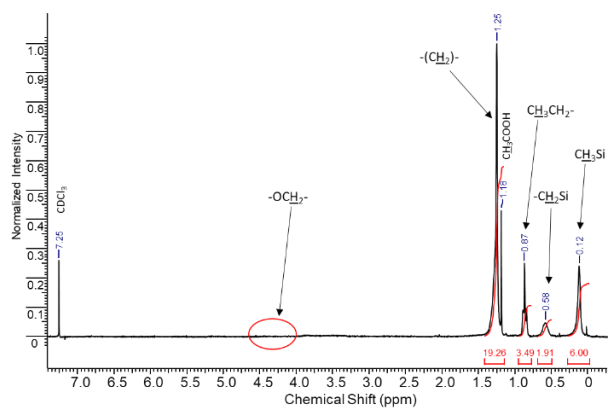
Figure 1. ^{1}H NMR spectrum of a sample of the reaction mixture after complete conversion of alkoxy groups for the MQ resin with 1:3 ratio of the units.
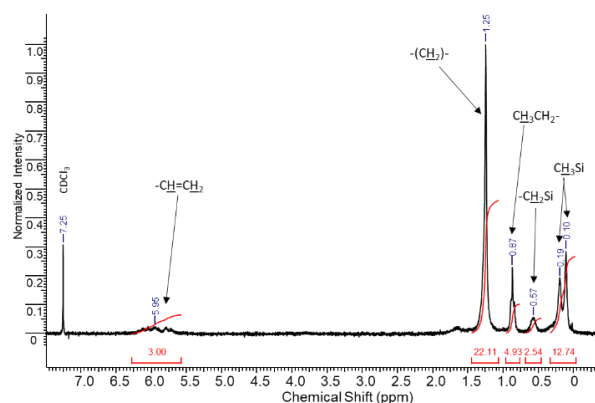
To determine the content of residual silanol groups in the MQ resins as well as to analyze the molecular-weight characteristics, they were blocked with chloro(dimethyl)vinylsilane in the presence of pyridine as an acceptor according to the known method (Scheme 2).
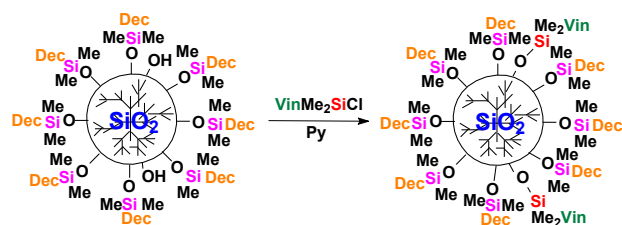
Scheme 2. Blocking of the decyl-containing MQ resins.

The content of residual silanol groups was calculated from the value of the integral intensity of vinyl group signals at 5.5–6.5 ppm in the ^{1}H NMR spectra. Figure 2 shows an example of such a spectrum for the MQ resin with 1:4 ratio of the units.

The contents of silanol groups in all MQ resins explored are presented in Table 1.

The resulting MQ resins were analyzed by gel permeation chromatography (GPC). It was shown that an increase in the content of Q units leads to the growth of a molecular weight and, consequently, the silica core of nanogels. The width of the molecular weight distribution also increases. All the GPC curves were monomodal with a maximum at M_p region. A reduction in the molecular-weight characteristics on passing from MQ 1:2 to MQ 1:3, despite an increase in the content of Q units, can be rationalized by a change in the synthesis conditions, *i.e.*, a transition to a milder temperature regime and the absence of an excess of acetic acid to prevent the product gelation. The main molecular-weight characteristics are presented in Table 1.

**Table 1.** Characteristics of the resulting MQ copolymers (M_W/M_N is the polydispersity index)

M/Q	M_N	M_W	M_W/M_N	M_p	Si–OH, %
1:2	6550	14150	2.16	7650	2.4
1:3	4600	9300	2.02	2850	4.9
1:4	33400	105700	3.16	16650	4.8

Morphology

The introduction of a filler into a polymer matrix by mixing from a solution ensures uniform distribution of the additive. However, at a high filler content (30 wt %), the particle aggregation becomes inevitable. Figure 3 shows micrographs of the PI compositions and copolymers with different M/Q ratios. The sizes of the filler particles (light regions) range from 1–2 to 50–70 μm. Notably, the average particle size decreases with the increasing content of Q units. In other words, the samples with 1:3 and 1:4 ratios are less prone to aggregation in the polymer matrix.

Rheological behavior

The original polyisoprene exhibits Newtonian behavior, *i.e.*, its viscosity remains constant over a wide range of applied shear stresses (Fig. 4). The viscosity of the filled compositions bearing 30 wt % of the MQ copolymers expectedly increases and exceeds the viscosity of the polymer matrix ~10 times. At that the shapes of the curves change. For the mixture with M/Q = 1:2, flow has a marked non-Newtonian character: a continuous decrease of the viscosity is observed with an increase of the shear stress. Similar behavior was detected for the sample of the copolymer with M/Q = 1:3. The behavior of the composition
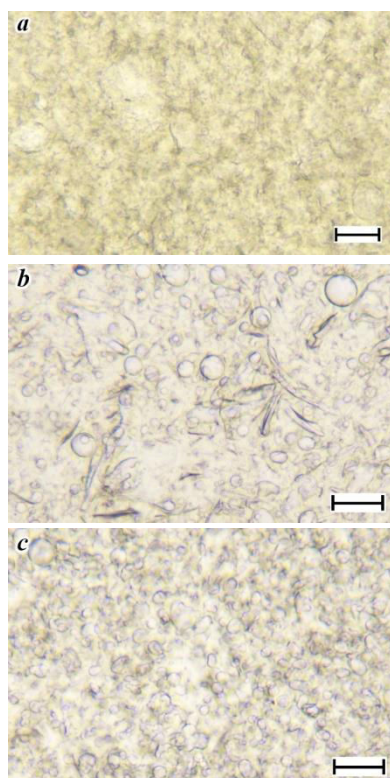
Figure 3. Micrographs of the compositions based on PI and the MQ copolymers (30 wt %). The segment size corresponds to 50 μm. M/Q ratio: 1:2 (*a*), 1:3 (*b*), 1:4 (*c*).

containing the copolymer with M/Q = 1:4 remains closest to the Newtonian one. Thus, from the viewpoint of rheological behavior, the most interesting filler is the copolymer in which the ratio of M and Q units is equal to 1:4. The compositions with this copolymer exhibit an almost linear flow pattern, which indicates the absence of structuring in the system, which is characteristic of highly filled systems.
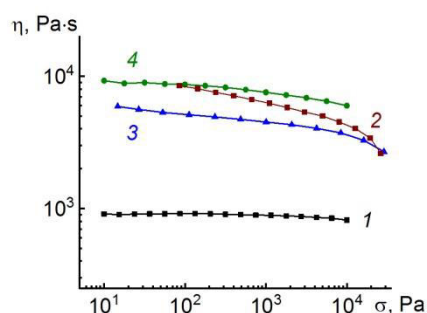

Figure 4. Dependence of the viscosity on the shear stress for the matrix polymer (*1*) and its compositions containing 30 wt % of the MQ copolymer with the M/Q ratio of 1:2 (*2*), 1:3 (*3*), and 1:4 (*4*).

The additional information about the nature of the structure formation in the compositions can be obtained by oscillatory measurements.

NMPI-500 polymer is a viscoelastic material, which is typical for rubbers [20]. At room temperature, viscous behavior prevails at low frequencies, *i.e.*, the loss modulus exceeds the elastic modulus. At frequencies above ~190 rad/s, the elastic component exceeds the viscous one. The introduction of the MQ copolymers into the polymer matrix naturally leads to an

increase in the absolute modules values without changing the general character of frequency dependences (Fig. 5). A transition through the crossover point ($G' = G''$) occurs slightly earlier: at a frequency of ~100 rad/s.
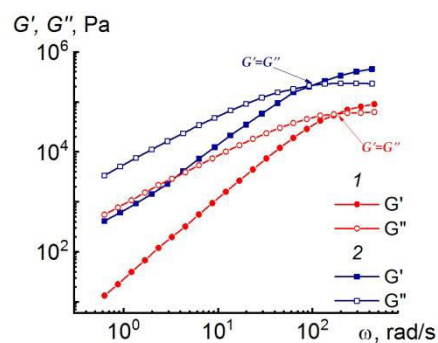
Figure 5. Frequency dependences of the dynamic moduli for polyisoprene (*1*) and its composition with 30 wt % of the MQ copolymer 1:4 (*2*).

An important characteristic of the MQ copolymers, from the viewpoint of their potential application as reinforcing fillers, is the extent of their effect on the mechanical characteristics of the cured composition. To obtain cross-linked rubbers, in this work a non-isothermal mode of rubber cross-linking across double bonds was used. Figure 6 shows the evolution of the elastic modulus depending on the temperature during cross-linking of the compositions under investigation.
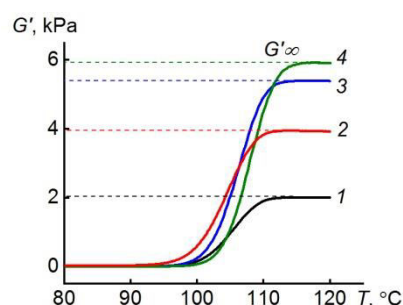
Figure 6. Variation of the elastic modulus during curing of NMPI-500 (*1*) and its compositions with the MQ copolymer with 1:2 (*2*), 1:3 (*3*), and 1:4 (*4*) ratio of the units.

The active cross-linking process occurs in the temperature range of 95–115 °C. Under these conditions, a drastic increase in the moduli is observed: from several thousands to several hundreds of thousands of pascals. Upon completion of the cross-linking process, the modulus value reaches a plateau, G'_∞. For all cross-linked compositions with the MQ copolymers, the modulus value on the plateau is significantly higher than that for the cross-linked rubber without a filler. The highest G'_∞ value was obtained for a system based on the MQ resin 1:4. The elastic modulus of this composition increases threefold compared to the unfilled rubber (Table 2).

Table 2. Elastic moduli of the cross-linked compositions based on NMPI-500 and the MQ copolymers

Sample	1	2	3	4
M/Q	–	1:2	1:3	1:4
G'_∞, kPa	2.0	3.9	5.4	5.9

Experimental section

Materials

Reagent grade tetraethoxysilane, methyl *tert*-butyl ether (MTBE), toluene, acetic acid, hexamethyldisiloxane, pyridine (Komponent-reaktiv, Russia), 1-decene (Vekton, Russia), tetramethyldisiloxane, chloro(dimethyl)vinylsilane (Aladdin, China), and Karsted's catalyst in the form of the platinum complex with divinyltetramethyldisiloxane in xylene (ABCR, Germany) were purchased from commercial sources and used without purification.

To obtain the model compositions, NMPI-500 polyisoprene (OAO EZSK, Russia) was chosen as a polymer matrix. The rubber features low molecular weight ($5.5 \cdot 10^4$) and relatively low viscosity (500 Pa·s at $T = 38$ °C).

To cross-link the compositions based on polyisoprene, quinol ether EKh-1 *O,O'*-bis(1,3,5-tri-*tert*-butyl-4-oxo-2,5)cyclohexadienyl-*p*-benzoquinone dioxime (*TU (Specifications) 6-09-11-2151-94*, OOO Angara-Reaktiv) was used. The derivatives of *p*-quinone dioxime mix with polymers and are effective low-temperature cross-linking agents for the compositions based on unsaturated rubbers [21–23]. EKh-1 powder was introduced into the composition in the amount of 5 wt parts per 100 wt parts of the rubber.

Syntheses

Synthesis of 1,3-didecyl-1,1,3,3-tetramethyldisiloxane. Karsted's catalyst (0.9 mL) was added to a mixture of tetramethyldisiloxane (200 g, 1.49 mol) and 1-decene (460 g, 3.28 mol). The reaction mixture was heated at 60 °C for 10 h until the disappearance of the signals of double bonds in the ^{1}H NMR spectrum. Then, the resulting mixture was diluted with toluene (1 L) and passed through a layer of silica gel to remove the catalyst. The solvent was removed under vacuum. The residue obtained was distilled at 1 mm Hg. The target product was collected as a fraction with a boiling point of 201–202 °C (99% purity). Yield: 550 g (89%).

Synthesis of decyl-containing MQ resin 1:2. A mixture of tetraethoxysilane (80 g, 0.384 mol), didecyltetramethyldisiloxane (40 g, 0.096 mol), acetic acid (280 g, 4.670 mol), and acetyl chloride (0.4 mL) was heated over an oil bath at 125 °C for 15 h. After addition of MTBE (0.5 L), the resulting mixture was washed with water until neutral reaction. The organic layer was separated, dried over anhydrous sodium sulfate, and evaporated to dryness (50–60% of a dry residue). Yield: 98%. The content of residual silanol groups determined by the blocking reaction was 2.4 wt %.

Synthesis of decyl-containing MQ resin 1:3. Tetraethoxysilane (60.2 g, 0.290 mol) and didecyltetramethyldisiloxane (20.0 g, 0.048 mol) were added to a mixture of acetic acid (69.4 g, 1.160 mol) and sulfuric acid (0.12 mL). The stirred reaction mixture was heated over an oil bath at 80 °C for 19 h. After addition of MTBE (0.5 L), the resulting mixture was washed with water until neutral reaction. The organic layer was separated, dried over anhydrous sodium sulfate, and evaporated to dryness (40–50% of a dry residue). Yield: 96%. The content of residual silanol groups determined by the blocking reaction was 4.9 wt %.

Synthesis of decyl-containing MQ resin 1:4.

Tetraethoxysilane (80.2 g, 0.390 mol) and didecyltetramethyldisiloxane (20.0 g, 0.048 mol) were added to a mixture of acetic acid (92.6 g, 1.540 mol) and sulfuric acid (0.16 mL). The stirred reaction mixture was heated over an oil bath at 80 °C for 21.5 h. After addition of MTBE (0.5 L), the resulting mixture was washed with water until neutral reaction. The organic layer was separated, dried over anhydrous sodium sulfate, and evaporated to dryness (40–50% of a dry residue). Yield: 95%. The content of residual silanol groups determined by the blocking reaction was 4.8 wt %.

Blocking the MQ resins with chloro(dimethyl)vinylsilane. To determine the content of residual silanol groups, a sample of the MQ resin (1 g) was dissolved in MTBE (30 mL). Then pyridine (2 mL) and chloro(dimethyl)vinylsilane (1.2 mL) were added. The reaction mixture was refluxed for 2 h and, after cooling to room temperature, washed with water until neutral reaction. The organic layer was separated and dried over anhydrous sodium sulfate. The volatile components were removed under vacuum at 1 mm Hg. The content of residual silanol groups was determined by the intensity ratio of the vinyl group proton signals at 5.5–6.5 ppm in the ^{1}H NMR spectra.

Method for the sample preparation

The MQ copolymers were introduced into the polymer matrix by mixing from a solution using a vacuum rotary evaporator. The rubber was preliminarily dissolved in MTBE in a PSB-Gals ultrasonic bath (operating frequency 60 kHz). Then a solution of the MQ copolymer in MTBE was added. The mixture was evacuated at 60 °C for 2–3 h on a Rotavapor rotary evaporator (Buchi, Switzerland) at 1 mm Hg. Mixing through a solution ensures more uniform distribution of the components in the polymer matrix.

For each of the copolymers, the mixtures with the filler content of 30 wt % were prepared.

Methods

The ^{1}H NMR spectra were recorded on a Bruker WP-250 SY spectrometer. The ^{29}Si NMR spectra were recorded on a Bruker Avance II 300 spectrometer with an operating frequency of 300 MHz. The chemical shifts in the ^{1}H NMR spectra were determined relative to *d*-chloroform ($\delta = 7.25$ ppm). The spectra were processed using the ACDLABS software package.

The analytical GPC was carried out on a chromatographic system consisting of a Styer series 2 high-pressure pump (Akvilon, Russia), a RIDK 102 refractive index detector (Czech Republic), a JETSTREAM 2 PLUS column thermostat (KNAUER, Germany), columns with a length of 300 mm and a diameter of 7.8 mm, filled with Phenogel sorbent (Phenomenex, USA) with a particle size of 5 mm and a pore size of 10^4 and 10^5 Å (with a separation range of up to 500000 and 1000000 D, respectively). THF was used as an eluent at a flow rate of 1.0 mL/min. The data recording and calculation were carried out using the MultiChrom program (Ampersand Ltd.) with the assignment of molecular weights relative to polystyrene standards.

The morphology of the filled systems was studied using a Biomed 6 PO laboratory optical microscope (Biomed-servis, Russia).

The rheological tests were carried out using a MARS 60 rotational rheometer (Thermo Scientific HAAKE, Germany). A cone-plane working unit was with a cone diameter of 20 mm (an angle between the cone generatrix and the plane was 1°). The tests were carried out under stationary flow conditions in the controlled shear stress mode and in the oscillation mode. The test temperature was 25 °C. The cross-linking kinetics was studied under non-isothermal conditions when the sample was heated from 50 to 120 °C at a constant rate of 1 deg/min with a strain amplitude of 1% at a frequency of 10 rad/s.

Conclusions

The MQ copolymers with decyl terminal groups and different M/Q ratios (1:2, 1:3, and 1:4) were synthesized. The synthesis conditions ensured obtaining the products, including the MQ resin, featuring a high content of inorganic component, soluble in many organic solvents. This made it possible to introduce the filler into the polymer matrix by mixing in solution and to obtain homogeneous mixtures.

The morphological studies of the resulting compositions allowed for determining the main features of the filler distribution in highly filled mixtures with the low-molecular weight carbon-chain rubber. It was shown that the best mixing was achieved for the resin with the M/Q ratio of 1:4.

The analysis of the rheological behavior of the compositions based on the rubber and the resulting MQ resins showed that the most promising filler is the copolymer with the M/Q ratio of 1:4. These compositions retain Newtonian behavior over a wide range of shear rates and stresses, and the cross-linked composites based on them feature the highest elastic modulus values.

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