Synthesis and Characterization of MQ Silicone Resins

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ABSTRACT: MQ silicone resins, which represent a broad range of hydrolytic condensation products of monofunctional silane (M) and tetrafunctional silane (Q), were synthesized by reaction of water glass with hexamethyldisiloxane. The optimum reaction time and the optimal reaction temperature is 30 min and 30–40°C, respectively. Concentrated hydrochloric acid is the best one among those catalysts tested. In large-scale experiments (420–1680 mL), the favorable feeding order is catalyst first, and then water glass, the mixture of hexamethyldisiloxane and ethanol last and most MQ silicone resin was observed. The structure of MQ silicone resin was characterized by FT-IR and GPC spectra. The MQ silicone resin shows narrow molecular weight distribution and the number average molecular weight of MQ silicone resin is 2917. The silicone pressure sensitive adhesive prepared from as-synthesized MQ resin has good tack (29#) and 180° peel adhesion (5.630*N*/20 mm). © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: MQ silicone resin; hexamethyldisiloxane; water glass; hydrolytic condensation reaction; gel formation

INTRODUCTION

MQ silicone resins represent a broad range of hydrolytic condensation products of monofunctional silane (M) and tetrafunctional silane (Q). MQ silicone resins of molecular weight in the range of 1000–10,000 are very useful in using as pressure sensitive adhesives,[1–6] silicone rubbers, coatings, additives and so on.[7–14] MQ silicone resins are mainly synthesized from water glass or ethyl silicate.[15] Ethyl silicate is less reactive than water glass, therefore, when ethyl silicate is used as starting material, the structure of MQ resins can be controlled easily and gel formation can be avoided effectively. However, ethyl silicate is expensive, resulting in limitations to its wide application in preparing MQ silicone resins. In contrast, water glass is cheap and readily available.[10,16,17] More recently, water glass and hexamethyldisiloxane (HMD) have been used as starting materials for the synthesis of MQ silicone resins.[16–19] Improvements have been made in better control of structure parameters such as molecular weight and its distribution.[16] However, little research has been devoted to increase MQ silicone resin yield by controlling gel formation. And the preparation of MQ silicone resins can be found most in the patent literature.[20–26] We synthesized MQ silicone resin by reaction of water glass with hexamethyldisiloxane. The factors influencing synthetic reaction of MQ silicone resin were described concretely. Finally, the best technical conditions were established. It would be helpful in avoiding gel, especially in large-scale experiments. The MQ silicone resins can be used for silicone pressure sensitive adhesives.

EXPERIMENTAL

Chemicals and reagents

Hexamethyldisiloxane (HMD) was purchased from Zhejiang Kaihua Synthetic Material (Zhejiang, China; bp, 100°C). Water glass, produced by Beijing Hongxing Guangsha Chemical Industry and Build Material Limited Liability Company (Beijing, China), was an aqueous solution with 28.66% silicon dioxide and 8.80% sodium oxide. Concentrated hydrochloric acid, concentrated sulfuric acid, acetic acid, toluene, and calcium chloride were chemical reagents from Beijing Chemical Factory (Beijing, China).

Preparation of MQ resin

In a three-necked flask equipped with a stirrer and a thermometer, the mixture (40 mL) of water glass and tap water (their volume ratio was 1 : 3) was charged. Under vigorous stirring, the catalyst (15 mL) and a mixture (155 mL) of HMD and ethanol (their volume ratio was 25 : 6) were successively added into the flask at a set temperature. About 5 min later, the transparent yellow–green solution

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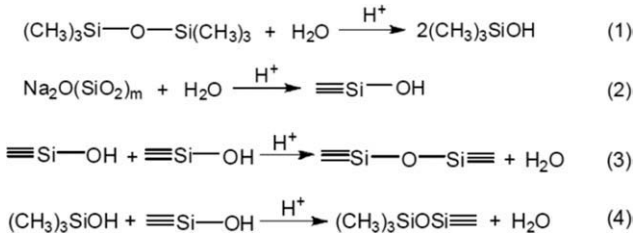

Figure 1 Synthesis reaction equation of MQ silicone resins.

turned into a white emulsion. Continued stirring for a given time, the reaction was stopped by stop heating and stirring. After standing for a few minutes, the emulsion separated into an organic phase and an aqueous phase. The organic phase was dried over calcium chloride. Then alcohol and excess HMD were removed under vacuum at 70°C. A white, friable and powdery solid, namely MQ silicone resin, was obtained.[7,16,18,20] The resin was completely soluble in solvents such as toluene and xylene. Characterization was conducted using the fresh samples, which were stored not over 2 weeks. Synthesis reaction equation of MQ silicone resins is shown in Figure 1.

Preparation of PSA

In a three-necked flask equipped with a stirrer and a thermometer, MQ silicone resin solution in toluene, 107 silicone rubber and triethylamine were proportionally charged. Under vigorous stirring and heating between 30 and 40°C, they were kept in reflux condition for 5 h and the reaction was stopped. Toluene solution of silicone pressure sensitive adhesive was obtained. Toluene and triethylamine was removed under vacuum at 65°C. Under stirring, silicone pressure sensitive adhesive was dissolved in ethyl acetate. Silicone pressure sensitive adhesive solution in ethyl acetate was coated on a dry film of 50 μm thickness and dried at 110°C in thermostatic air-blower-driven drying closet for 6 h. The films were conditioned 24 h prior to testing at 23 ± 2°C and 50 ± 2% relative humidity.

Characterization of MQ resin

The molecular weight and its distribution of MQ resin was determined by Water 717-2410-996 gel permeation chromatography (Water, USA), using THF as an eluent and polystyrene as the standard. The FTIR spectra were recorded on a Nicolet 50XC spectrometer (Nicolet, USA) and scanned between 400 and 4000 cm^{-1}.

Characterization of PSA

Pressure sensitive adhesive tapes (50-μm thick) were used in the following experiments. Stainless steel panels were used as substrates in all tests.

Tack of test samples was determined with CZY-G Primary Adhesive Tester (Jinan Lan'guang M and E Technology, China). The testing process of tack as follow: The specimen was cut into 100 × 100 mm^2. The rolling ball test apparatus was placed on one end of the specimen. The different stainless balls were released from the top of the apparatus. The maximum number of the ball could be stopped was recorded. Three specimens were tested per sample.

Holding power of test samples was measured with CZY-6S Lasting Adhesive Tester (Jinan Languang M and E Technology, China). The samples were cut into 25 × 100 mm^2 and laminated against a stainless steel substrate using a 2000 g rubber coated roller. Dwelling time was 1 min. The test samples were dragged using a 1000 g weight. The time that the test samples fell off was recorded.

About 180° peel adhesion was performed on a material testing instrument (HY-590S, Taiwan). The testing process of 180° peel adhesion as follow: The samples were cut into 20 × 200 mm^2 and laminated against a stainless steel substrate using a 2000 g rubber coated roller. Dwelling time was 1 min. The testing speed of a tensile tester was 200 mm/min. The average force per 10 mm to peel the specimen from the substrate was reported. Three specimens were tested per sample.

RESULTS AND DISCUSSION

Effect of temperature

Table I shows the effect of reaction temperature on the reaction of water glass with HMD. Reaction time was 30 min, and catalyst was concentrated hydrochloric acid. It was seen that the MQ resin yield was greatly affected by reaction temperature. When the reaction temperature was below 30°C, no product was obtained. At 30–40°C, 7.5 g MQ silicone resin was generated and no gel formed. However, with further increase of the reaction temperature, a great

TABLE I
Effect of Reaction Temperature on the Reaction

Reaction temperature	30°C below	30°C	40°C	50°C	70°C	90°C
Gel	No gel	No gel	No gel	Gel	A lot of gel	A lot of gel
Value of product (g)	0	7.5	7.5	3.0	0	0

TABLE II
Effect of Reaction Time on the Reaction

Reaction time	10 min	20 min	30 min	1 h	2 h	4 h
Gel	No gel	No gel	No gel	No gel	No gel	No gel
Value of product (g)	6.0	7.0	7.6	7.6	7.6	7.6

TABLE III
The Effect of Catalysts on the Reaction

Catalyst	Concentrated hydrochloric acid	Concentrated sulphuric acid	Acetic acid
Gel	No gel	A lot of gel	A lot of gel
Value of product (g)	7.6	0	0

amount of gel was produced, resulting in no product generation.

When temperature was low, the reactions did not take place because they could not be triggered at low temperature. However, very high temperature would result in gelation because of crosslinking reaction between siloxane chains [eq. (3)]. Therefore, the optimum temperature is determined as 30–40°C.

Effect of time

The effect of reaction time on the reaction at 35°C was represented in Table II. It could be observed that when reaction time increased from 10 to 30 min, the MQ resin yield increased from 6.0 to 7.6 g. However, when reaction time further increased from 30 min to 4 h, the MQ resin yield became constant. It was supposed that as the reaction was carried out for 30 min, the reaction had gone to completion. The optimal reaction time is hence determined as 30 min.

Effect of catalyst

To investigate an influence of catalyst on the reaction, we used concentrated hydrochloric acid, concentrated sulfuric acid and acetic acid as catalysts, respectively, for the synthesis of MQ silicone resins. Reaction temperature and reaction time were 35°C and 30 min, respectively. When concentrated hydrochloric acid was used as catalyst, MQ resin yield was higher and no gel was generated, as shown in Table III. The catalyst of concentrated sulfuric acid or acetic acid easily lead to gelation and no product was obtained.

HMD was the source of monofunctional unit [eq. (1)][13,16]. Hydroxyl-terminated siloxane chains were formed by reaction eq. (2). End-capping reaction of siloxane chain with monofunctional unit produced MQ silicone resin [eq. (4)]. Crosslinking reaction between siloxane chains formed gel [eq. (3)]. If end-capping reaction was not fast enough, the crosslinking reaction would lead to gel formation and less or even no MQ resin was generated. In contrast, if the end-capping reaction was much faster than crosslinking reaction, no gel was produced and MQ silicone resin with high yield was obtained.

Concentrated sulfuric acid could accelerate the crosslinking reaction rate of siloxane chains, resulting in gelation. Acetic acid with weak acidity could not catalyze end-capping reaction, while the crosslinking reaction could take place. Thus, concentrated hydrochloric acid is the best catalyst among these catalysts in the reaction of water glass with HMD.

Effect of feeding order

As shown in Table IV, in small-scale experiment (210 mL), there was no difference in MQ silicone resin yield when different feeding orders were applied. For large-scale experiments (420–1680 mL), the second feeding order was better than the first. Increase of MQ resin yield was proportional to experimental magnification times by the second feeding order. However, when the first feeding order was applied, larger-scale experiment would lead to more gel formation.

At the initial phase of the reactions, high concentration of catalyst was in favor of end-capping reaction, while low concentration of catalyst accelerated crosslinking reaction causing gelation. When added water glass solution into the catalyst, the instantaneous concentration of catalyst was from the highest concentration to a steady value. While added catalyst into the water glass solution, instantaneous concentration of catalyst increased gradually, and finally

TABLE IV
Effect of Feeding Order on Reaction

Feeding order		Small-scale experiment	Large-scale experiments		
			2 times	4 times	8 times
Feed water glass first, then catalyst, the mixture of HMD and ethanol last	Gel	No gel	Gel	Gel	A lot of gel
	Value of product (g)	7.5	2.0	0	0
Feed the catalyst first, then water glass, the mixture of HMD and ethanol last	Gel	No gel	No gel	No gel	No gel
	Value of product (g)	7.5	15.0	30.0	60.0

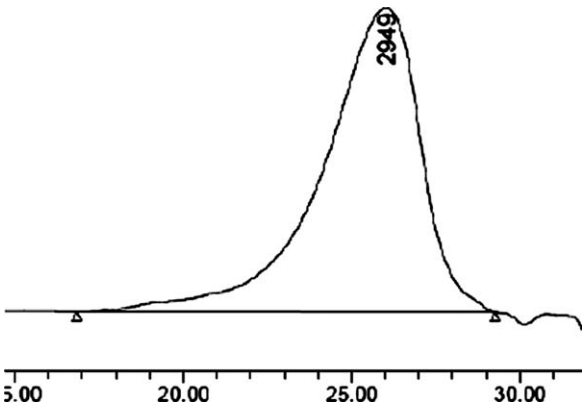

Figure 2 GPC chromatogram for the MQ silicone resin. The reaction conditions are: temperature (35°C), reaction time (30 min), and catalyst was concentrated hydrochloric acid.

arrived the steady value, which more easily led to gelation. Thus, the optimum feeding order is the second feeding order.

GPC analysis

Molecular weight and molecular weight distribution of MQ resin was analyzed by GPC (Fig. 2). The reaction conditions: reaction temperature was 35°C, reaction time was 30 min, and catalyst was concentrated hydrochloric acid, feeding order was the catalyst first, then water glass, the mixture of HMD and ethanol last. Figure 2 shows that the MQ resin had a monomodal and narrow molecular weight distribution. The number average molecular weight of MQ resin was 2917.

FT-IR analysis

The structure of MQ silicone resin was examined by FTIR, as shown in Figure 3. The reaction conditions: reaction temperature was 35°C, reaction time was 30 min, and catalyst was concentrated hydrochloric acid, feeding order was the catalyst first, then water glass, the mixture of HMD and ethanol last. The broad absorption at 3487.2 cm^{-1} was attributed to O—H stretching vibration of Si—OH. The sharp-medium intensity band at 2901.6 cm^{-1} was due to CH_3. Absorption at 1083.6 cm^{-1} suggested the presence of Si—O—Si. The characteristic absorption of Me_3SiO were 756.9, 844.4, and 1254.5 cm^{-1}.

Properties of PSA

The basic properties of the silicone pressure sensitive adhesive tape were as follows:

- Tack: 29#.
- Holding power: 2164 s.
- 180° peel adhesion: 5.630*N*/20 mm.

It was seen that the synthesized MQ resin could be used for pressure sensitive adhesives and the silicone pressure sensitive adhesive tape had satisfactory peel

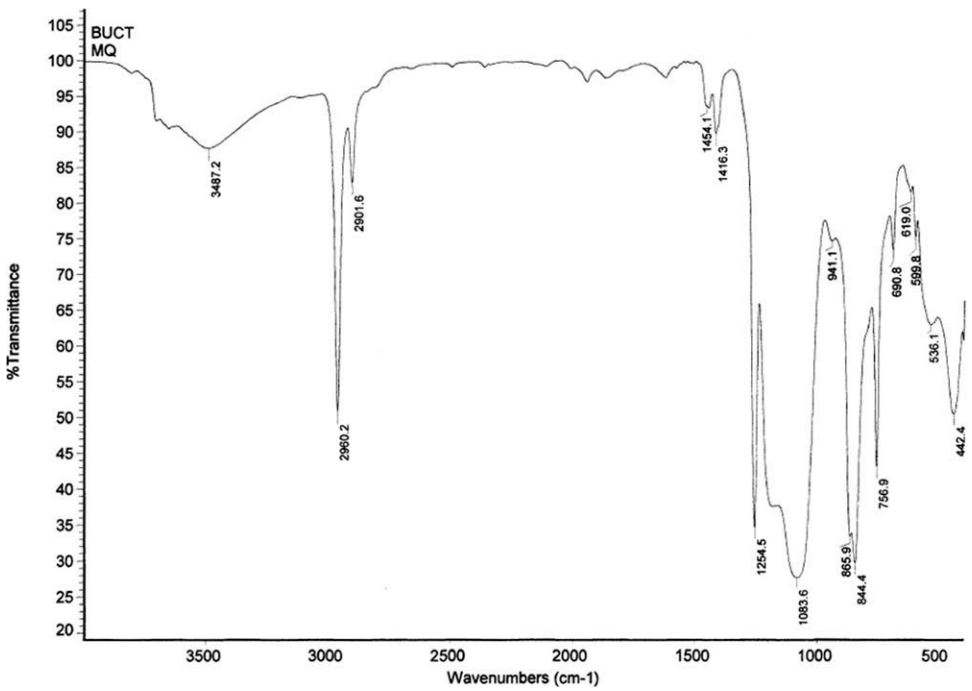

Figure 3 FTIR spectrum of the MQ silicone resin. The reaction conditions are: temperature (35°C), reaction time (30 min), and catalyst was concentrated hydrochloric acid.

strength and tack, but the holding power need to be improved.

CONCLUSION

Here we synthesized MQ silicone resin from water glass and HMD. Concentrated hydrochloric acid is the best catalyst among those tested. The reaction time in 30 min and the reaction temperature at 30–40°C were determined as the optimal synthesis conditions of MQ silicone resin. In large-scale experiments (420–1680 mL), the favorable feeding order is catalyst first, and then water glass, the mixture of hexamethyldisiloxane, and ethanol last. The MQ silicone resin shows a monomodal and narrow molecular weight distribution. Pressure sensitive adhesive made from the synthesized MQ resin and silicone rubber had good performance, which proved that the MQ silicone resin can be applied in pressure sensitive adhesives.

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