Preparation and characterization of silicon rubber with high vinyl contents

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Abstract

Based on anionic ring-opening polymerization, vinyl silicon rubber (VSR) raw rubber with vinyl contents of 2.81%, 4.86%, 6.06% and 7.90% was prepared by using tetramethylammonium hydroxide (Me4NOH) as catalyst. Effect of amount of catalysts and capping agent on molecular weight and viscosity of VSR raw rubber was discussed. Based on the orthogonal test method, an optimal formulation with a catalyst amount of 0.08 g and a capping agent of 0.08 mL for VSR raw rubber was obtained. The characterization of FTIR confirmed that VSR raw rubber was successfully prepared, and the vinyl content was consistent with the results of the iodobromo method. The preparation method of the VSR raw rubber is simple in operation, and the catalyst is easy removed and has no pollution to the organic silicon products.

Keywords

Vinyl Silicon Rubber; Ring-opening Polymerization; Aaw Rubber; Silicon Rubber.

1. Introduction

Silicon Rubber (SR), as a linear silicone, which has many excellent properties (such as, high or low temperature resistance, weather resistance, chemical resistance, gas permeability, non-toxicity, biocompatibility, etc), have good application prospects in the fields of aerospace, electronics, and medical equipment [1-3]. However, unmodified SR can normanlly not meet with commercial application due to poor membrane-forming, mechanical strength, and thermal conductivity [4-6]. Therefore, some modified methods reported in some literatures were used to improve those performance [7-9].

The introduction of vinyl groups into SR is good modified method because of more functional groups and better membrane-forming properties. At present, vinyl silicon rubber (VSR) can be prepared by anionic polymerization and cationic polymerization. However, preparation method of anionic polymerization is often used because the process of cationic polymerization method is complex and the post-processing is difficult. Anionic polymerization method is commonly used potassium hydroxide (KOH) or tetramethyl ammonium hydroxide (Me_4NOH) as the catalysts. But cheap KOH as catalyst possesses low catalytic efficiency and difficult post-processing.

In the paper, VSR raw rubber with different vinyl contents was prepared by anionic ring-opening polymerization with tetramethylammonium hydroxide (Me_4NOH) as catalyst. Effect of amount of catalysts and capping agent on molecular weight and viscosity of VSR raw rubber was discussed. The chemical structure of the VSR raw rubber was also characterized by FTIR.

2. Experimental Procedure

2.1 Materials

Divinyl tetramethyl disiloxane (MM^{Vi}), octamethyl cyclotetrasiloxane (D_4) and tetravinyl tetramethylcyelo tetrasiloxane (D_4^{Vi}) was obtained from Guangzhou shuangtao fine chemical co., Ltd (China). tetramethyl ammonium hydroxide (Me_4NOH) was purchased from Tianjin daomao chemical reagent factory, china. All other chemicals were of analytical grad and used without further purification.

2.2 Preparation of VSR raw rubber

Synthesis of Me_4NOH phenolate: 2.4 g 25% (mass fraction) Me_4NOH aqueous solution added into 100 mL three-necked flask was dehydrated for 15 min through the rotary evaporation apparatus at 50 ℃. The resulted white powder Me_4NOH and 24.0 g D_4 were mixed and stirred for 2 h and under N_2 to form translucent Me_4NOH phenolate.

A certain proportion of D_4 and D_4^{vi} added into 100 mL three-necked flask was dehydrated for 15 min through the rotary evaporation apparatus at 90 ℃. Then MM^{vi} and Me_4NOH phenolate were added into the three-necked flask and the mixture were reacted for 2 h under N_2. When the viscosity of VSR raw rubber had no change, the mixture system was heated to 140 ℃ to remove unreacted Me_4NOH and heated to 160 ℃ to remove some impurities. The reaction process was shown in Fig. 1. By changing the ratio of D_4/D_4^{vi}, the VSR raw rubber with different vinyl contents were prepared.

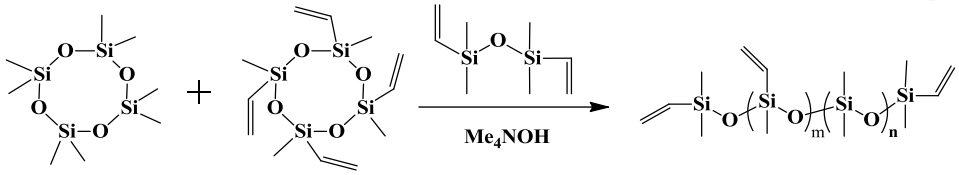

Fig. 1 Reaction process of VSR raw rubber

2.3 Measurement of vinyl contents

The vinyl content of VSR raw rubber was determined by iodine bromine method. The vinyl groups of VSR raw rubber dissolved in carbon tetrachloride were reacted with excessive IBr by the addition reaction. Then excessive I_2 reacted completely with unreacted IBr. Iodometry was operated by using 0.1 mol/L $Na_2S_2O_3$ standard solution and the titration volume of $Na_2S_2O_3$ standard solution was recorded as V_0. For control experiment, the titration volume of $Na_2S_2O_3$ standard solution was recorded as $V_{control}$. Every sample was tested three times under room temperature. The vinyl content of VSR raw rubber could be calculated according to the following formula.

$$(\text{vinyl content})\% = \frac{0.0005 C_{Na2S2O3}(V_{control} - V_0)M}{m_{sample}} \times 100\%$$

2.4 Characterization of chemical structure

Fourier transform infrared (FTIR) spectroscopy (BRUKER EQUINOX 55, Germany) was used to confirm the chemical structures of VSR.

3. Results and disscussion

3.1 Chemical structure of VSR

The chemical structure changes of the VSR raw rubber with different vinyl contents were monitored by FTIR and shown in Fig. 2. Stretching vibration absorption peak at 1089 cm^{-1} was characteristic peak of Si-O-Si. The vinyl groups (-CH=CH_2) characteristic peak at 1599 and 3057 cm^{-1} appeared. The results showed that the VSR raw rubber was prepared sucessfully. In addition, the characteristic peak of the VSR raw rubber with vinyl content of 2.81%, 4.86%, 6.06% and 7.90% were similar and the peak intensity at 1599 and 3057 cm^{-1} were increaed with vinyl contents.

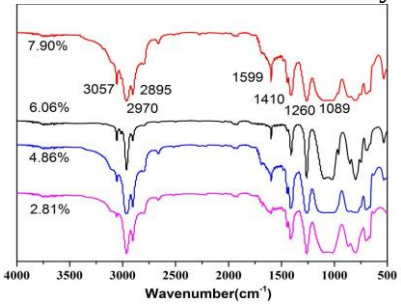

Fig. 2 FTIR spectra of VSR raw rubber with different vinyl contents

3.2 Effect of amount of catalysts on properties of VSR

VSR raw rubber with different vinyl contents was prepared by using D_4 and D_4^{Vi} as matrix materials, and Me_4NOH as catalyst, and MM^{Vi} as termination agent. The effects of amount of catalysts on properties of VSR raw rubber were shown in Table 1. It could be seen from the table that viscosity and molecular weight of VSR raw rubber were increased with an increasing of amount of catalysts in the case of fixed capping agent.

Table 1 Effect of amount of catalysts on properties of VSR raw rubber

amount of catalysts (g)	t/s	t_0/s	concentration (g/mL)	relative viscosity (η_r)	specific viscosity (η_{sp})	reduced viscosity (η_{sp}/c)	intrinsic viscosity ([η])	molecular weight (M_η)
0.10	143.0	96.25	0.00504	1.4857	0.48571	96.372	84.095	367208
0.09	155.5	96.25	0.00504	1.6156	0.61558	122.14	103.44	489534
0.08	161.3	96.25	0.00504	1.6758	0.67584	134.10	112.07	547210
0.07	145.0	96.25	0.00504	1.5065	0.50649	100.50	87.260	386548
0.06	125.6	96.25	0.00504	1.3049	0.30493	60.503	55.258	204937

Notes: D_4:D_4^{vi}=3:1，MM^{vi}=0.08 mL，temperature：95 ℃.

3.3 3.3 Effect of amount of capping agent on properties of VSR

For anionic polymerization system, capping agent is indispensable during chain termination phase. The effects of amount of capping agent on properties of VSR raw rubber were shown in Table 2. As can be seen from the table, viscosity and molecular weight of VSR raw rubber were decreased with an increasing of amount of capping agent in the case of fixed catalyst.

Table 2 Effect of amount of capping agent on properties of VSR raw rubber

amount of capping agent (mL)	t/s	t_0/s	concentration (g/mL)	relative viscosity (η_r)	specific viscosity (η_{sp})	reduced viscosity (η_{sp}/c)	intrinsic viscosity ([η])	molecular weight (M_η)
0.14	130.3	96.25	0.00528	1.3538	0.35377	67.001	60.414	231966
0.12	152.5	96.25	0.00528	1.5844	0.58442	110.68	94.393	431121
0.10	157.5	96.25	0.00528	1.6364	0.63636	120.52	101.60	477501
0.08	161.3	96.25	0.00504	1.6758	0.67584	134.10	112.07	547210
0.06	181.0	96.25	0.00528	1.8805	0.88052	166.77	133.65	698780

Notes: D_4:D_4^{vi}=3:1，amount of catalysts =0.08 g，temperature：95 ℃.

4. Conclusion

VSR raw rubber with different vinyl contents (2.81%, 4.86%, 6.06% and 7.90%) was prepared by using D_4 and D_4^{Vi} as matrix materials, and Me_4NOH as catalyst, and MM^{Vi} as termination agent. Amount of catalysts and capping agent had effect on the molecular weight and viscosity of VSR raw rubber. Based on the orthogonal test method, an optimal formulation with a catalyst amount of 0.08 g and a capping agent of 0.08 mL for VSR raw rubber was obtained.

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