Contents List available at VOLKSON PRESS

New Materials and Intelligent Manufacturing (NMIM)

DOI : http://doi.org/10.26480/icnmim.01.2018.149.151

Journal Homepage: https://topicsonchemeng.org.my/

ISBN: 978-1-948012-12-6

PREPARATION AND CHARACTERIZATION OF SIDE CHAIN EPOXY MODIFIED SILICONE OIL FOR PRECURSOR FIBER OF CARBON FIBER

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ARTICLE DETAILS

Article History:

Received 26 June 2018
Accepted 2 July 2018
Available online 1 August 2018

ABSTRACT

In the carbon fiber production process, the oil agent is a very important part that affects the quality of the carbon fiber, and the epoxy group can improve the heat resistance of the silicone oil, so the epoxy modified silicone oil can be used as an integral part of the carbon fiber precursor oil agent. In this article, the preparation and characterization of side chain epoxy modified silicon oil for precursor fiber of carbon fiber will be reported. There were two major steps to prepare epoxy modified silicone oil. In the first step, low hydrogen silicone oils were synthesized by using octamethylcyclotetrasiloxane (D_4) and 1,3,5,7-tetramethylcyclotetrasiloxane (D_4^H) as starting materials, hexamethyldisiloxane (MM) as a capping agent and 98% sulfuric acid as a catalyst. In the second step, hydrosilylation method was used to synthesize the target product, low hydrogen silicone oils and 1,2-epoxy-4-vinylcyclohexane as a starting material and a chloroplatinic acid-isopropanol as catalyst. The synthetic epoxy modified silicone oil was characterized by IR and NMR spectra, which proved that both synthetic routing and its molecular structure was correct.

KEYWORDS

Epoxy group, Silicone oil, Oil agent, Hydrosilylation, Precursor fiber, Carbon fiber.

1. INTRODUCTION

Carbon fiber has been widely used in aerospace, advanced sporting goods, energy, civil construction, automobile manufacturing, and other general industrial fields because of its excellent specific strength, specific modulus and chemical stability. The most widely used at present is PAN-based carbon fiber and it occupies 90% on market. When acrylic precursor fiber converted to carbon fiber through multiple processing such as pre-oxidation at 250~300 ℃ in oxygen, carbonization at 300~2000 ℃ and graphitization at 2000~3300 ℃ in an inert atmosphere, oil agent was essential for eliminating adhered or fused PAN precursors and defect on precursors. More importantly, oil agent had a very significant impact on the smooth progress of the subsequent pre-oxidation and carbonization process and even the quality of the final carbon fiber product. Therefore, related research has always been one of the most concerned contents of various carbon fiber research and production units [1,2]. Since the modified polydimethylsiloxane oil has a good heat resistance, a small surface tension, a small viscosity-temperature coefficient, and a good film-forming property, it can be used as an oil agent in a carbon fiber manufacturing process. The modified groups mainly include amino groups, epoxy groups, and polyether chains. Amino group can improve the film-forming and hydrophilicity of oil agent, epoxy group can improve the heat resistance of oil agent, and polyether chain can improve the self-emulsification of oil agent. Their molecular structures are shown in Figure 1.

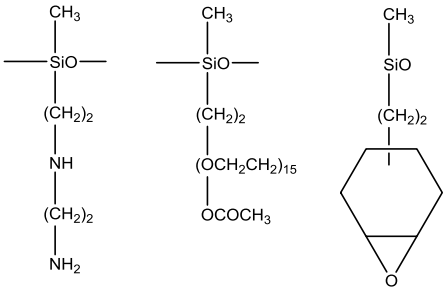


Figure 1: Structural Diagram of Modified Silicone Oil with Three Different Side Groups

Since the epoxy modified oil agent can improve the heat resistance, so that it can protect the fiber during pre-oxidation and low-temperature carbonization, our research group has intensified R&D of the epoxy-modified oil agent and would exploit its new discoveries such as self-emulsified cationic waterborne epoxy modified oil agent as well as integrated design of epoxy group, amino group and polyether chain into oil agent. In this paper, the preparation and characterization of side chain epoxy modified silicon oil for precursor fiber of carbon fiber will be reported. Low hydrogen silicone oils were synthesized by using D_4 and D_4^H as starting materials, MM as a capping agent and 98% sulfuric acid as a catalyst. The epoxy modified silicone oil was prepared by hydrosilylation method from low hydrogen silicone oils and 1,2-epoxy-4-vinylcyclohexane as a starting material and a chloroplatinic acid-isopropanol as a catalyst [3,4].

2. EXPERIMENTAL

2.1 Materials

Octamethylcyclotetrasiloxane (D_4) and 1,3,5,7-tetramethylcyclosiloxane (D_4^H) were purchased from Shenzhen Osbang new material co.,Ltd.

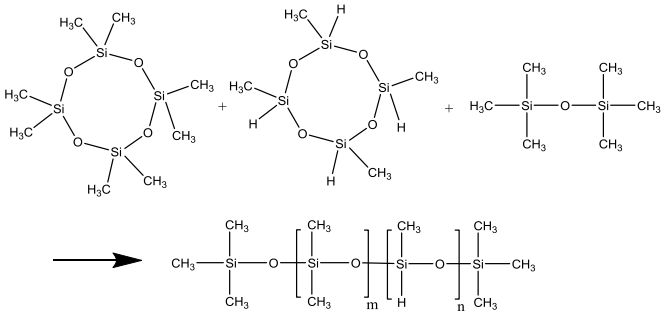
Hexamethyldisiloxane (MM) were products of the Shanghai Titan Technology Co., Ltd. 1,2-epoxy-4-vinylcyclohexane were purchased from Zhengzhou Alpha Chemical Co., Ltd. 98% sulfuric acid is produced in Xilong Scientific Co., Ltd. Analytical pure anhydrous sodium sulfate produced at the Tianjin yongda chemical reagent Co., Ltd. Isopropanol and chloro platinated acid were obtained from Liaoning Quanrui Reagent Co., Ltd.

2.2 Preparation of Catalyst

Isopropanol is dehydrated with anhydrous sodium sulfate for 24 hours and then filtrated to removal of inorganic impurities. 0.25 g of chloroplatinic acid was dissolved in 25 ml of dried isopropanol and stirred under N_2 at 45° C. to 50° C. for 1 h to 2 h to prepare a chloroplatinic acid-isopropanol catalyst. The chloroplatinic acid-isopropanol catalyst was placed in a refrigerator at 4°C for one week before use. The amount of chloroplatinic acid-isopropanol catalyst is 10ppm~15ppm of the total amount of reaction monomers [5,6].

2.3 Preparation of H-PDMS

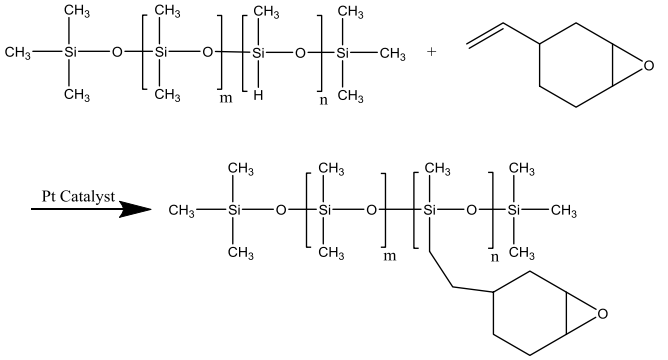
Referring to the literature, 250 ml four-neck reactor equipped with a stirrer and thermometer were added 21.18 g of D_4, 4.24 g of D_4^H, 0.5 g of MM and 1.5 ml of concentrated sulfuric acid. The reaction was carried out at 30°C for 8 h under nitrogen protection. Excess sodium bicarbonate was added, and negative-pressure filtration at the end of the reaction. After the unreacted reagentd evaporates, H-PDMS is obtained: molecular weight Mn=10000. Similarly, H-PDMS with Mn=2000-10000 can be prepared. The schematic of synthetic reaction is as following:



2.4 Preparation of EP-PDMS

In general, the synthetic method of epoxy-modified silicone oil is mainly divided into three categories: ①Hydrosilylation of hydrogenated silicone oils with terminal alkenyl epoxides; ②Polymerization of D_4, D_4^H; ③Other synthesis methods, such as α, ω-dihydroxy silicone oil and epichlorohydrin condensation reaction. In this paper, we synthesized side chain epoxy modified silicone oil by hydrosilylation [7].

In a four-neck reactor equipped with a thermometer, a stirrer, and a reflux condenser, a certain amount of xylene was used to dilute 1,2-epoxy-4-vinylcyclohexane, a small amount of ethanol and a catalyst were added, and the mixture was heated to 45°C. Adding hydrogen-containing silicone oil to the mixture. The reaction was carried out at 90 ℃ for 10 h under nitrogen protection. After the reaction is completed, xylene is distilled off under reduced pressure to obtain an epoxy-modified silicone oil. The schematic of synthetic reaction is as following:



3. RESULTS AND DISCUSSION

3.1 Physical Properties of the Product

The appearance of the product is colorless to light yellow transparent liquid.

3.2 FT-IR Spectra

FTIR spectra of EP-PDMS is compared with H-PDMS, the characteristic absorption peak of Si-H bond at 2152 cm^{-1} disappeared, indicating that the Si-H bond in the H-PDMS completely reacted with 1,2-epoxy-4-vinylcyclohexane to generate EP-PDMS. The absorption peak near 1095 ~ 1024 cm^{-1} is assigned to Si-O-Si; 1407 cm^{-1} and 872 ~ 736 cm^{-1} are characteristic absorption peaks of Si-CH_3; 2962 cm^{-1} is the peak of stretching vibration of epoxy C-H; there is no characteristic absorption peak of Si-H at 2250 ~ 2050 cm^{-1}; there is no bending vibration absorption peak of Si-H at 914 cm^{-1}, indicating that Si-H has undergone addition reaction with double bond (C=C), therefore Si-H has disappeared, and EP-PDMS has been prepared successfully. The FTIR spectra of H-PDMS and EP-PDMS is shown in Figure 2.

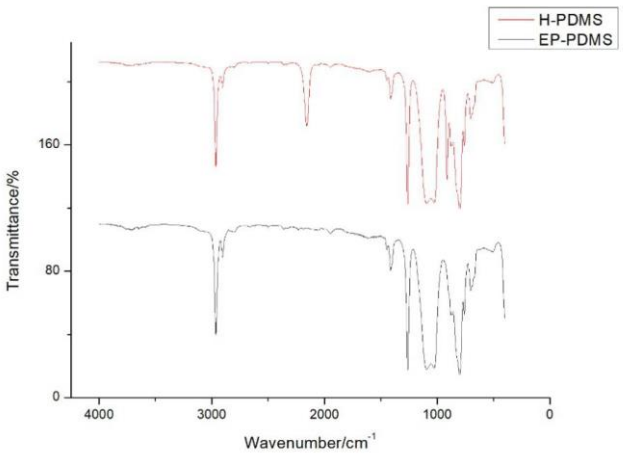


Figure 2: The FTIR Spectrum of the H-PDMS and EP-PDMS

3.3 H-NMR Characterization of the Product

The H-NMR of epoxy-modified silicone oil is shown in Figure 3.

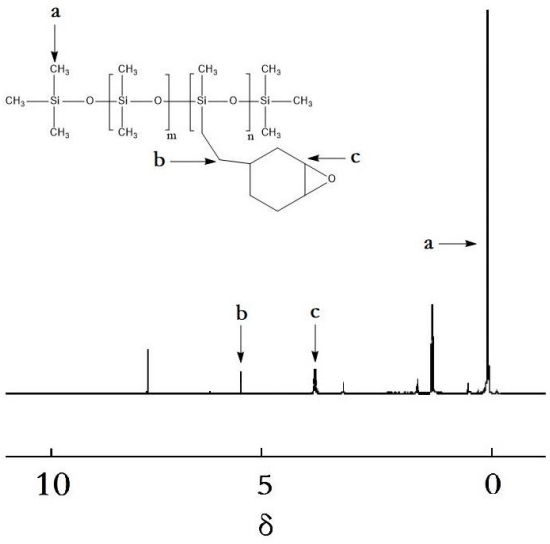


Figure 3: The H-NMR spectrum of the EP-PDMS

In Figure 3, δ = 0.5 is the chemical shift of hydrogen on Si-CH_2, and δ = 4.7 (4.68) is the chemical shift of hydrogen on Si-H; δ = 5.5 is a vinyl group; δ = 3.1 is the chemical shift of hydrogen on the epoxy C-H. According to comparison of H-NMR and FTIR spectra of EP-PDMS with H-PDMS, a conclusion is drawn that the target product has been synthesized, that is, the side chain epoxy modified silicone oil has been synthesized.

4. CONCLUSIONS

In this work, a two-step synthetic procedure of side chain epoxy modified silicone oil was developed. In the first step, low hydrogen silicone oils (H-PDMS) were synthesized by using D_4 and D_4^H as the starting materials, MM as a capping agent and 98% sulfuric acid as a catalyst. In the second step, hydrosilylation method was used to synthesize the target product (EP-PDMS), H-PDMS and 1,2-epoxy-4-vinylcyclohexane as a starting material and a chloroplatinic acid-isopropanol as catalyst. The synthetic epoxy modified silicone oil was characterized by FTIR and H-NMR spectra, which proved that both synthetic routing and its molecular structure was correct. The synthesized epoxy-modified silicone oils can be used for further processing to become the oil agent for the production of carbon fiber precursors.

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