

# Synthesis and characterization of polysiloxane containing methyl vinyl groups

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**Abstract—** Polymethylvinylsiloxane (PMVS) were prepared by pre-hydrolysis/condensation of methylvinylchlorosilane (MVDCS) and dimethyldichlorosilane (DMDCS) followed by catalysis equilibrium copolymerization by sulphuric acid ( $H_2SO_4$ ) and all manipulations in the experiments were performed under ambient condition. The PMVS were characterized by Fourier transform infrared spectroscopy (FTIR). This method has provided information about the structure of the polymer. Thermal properties of the polymethylvinylsiloxane were studied by using thermogravimetric analysis (TGA) indicate that the polymethylvinylsiloxane showed high thermal decomposition temperatures and low residue yields as a result of oxidation or degradation of methyl/vinyl groups.

**Keywords:** Polymethylvinylsiloxane; copolymerization, thermal decomposition

## I. Introduction

Polysiloxane compounds containing methyl vinyl group have characteristics of both inorganic and organic materials, and offer a number of advantages not found in other organic compounds. A main interest in polysiloxane containing these copolymers and silicone-modified networks is directly related to the interesting combination of properties offered by these materials, which include extremely high backbone flexibility and very low glass transition temperatures ( $T_g$ ), around  $-120^\circ C$ , good thermal and oxidative stability, high gas permeability, excellent dielectric properties, physiological inertness or biocompatibility as well as high stability towards heat, chemicals and UV radiation. Thus, methyl vinyl polysiloxane can be made into heat-resistance articles, and be used as sealing, shock proofing, insulating materials in aviation, navigation, instrument, electrical

equipment's, also be made into cold-or-heat-air transmission-tubes, cables, human organs, blood vessels, air penetrable films, as well as mold release agent used in rubber procession and precision casting [1- 6].

Polysiloxanes are known for excellent low temperature capabilities as well as chemical and thermal stability. Regardless their thermal stability, polysiloxanes tend to depolymerize at elevated temperatures due to random chain scission. In order to improve their long-term thermal stability at high temperature while still retaining their desirable low temperature flexibility, these research shall focus on structured modifications, among them are, the use of different structural units which were expected to successfully prevent formation of the linear or cyclic degradation products when incorporated into the polysiloxane backbone.

By using methylvinylsilicone gum instead of methylsilicone gum as the matrix gum, high strength vulcanizates can be obtained which show that vinyl groups have reactivity and can act as active centers in curing of silicone gum. Similarly, polysiloxanes containing different carbofunctional groups can be prepared from polysiloxanes containing vinyl groups [2,3].

However, few studies on the synthesis of polysiloxane with methyl vinyl have been reported considering their remarkable thermal properties. Moreover, the characteristics and mechanism of the degradation of such copolymers have not yet been thoroughly delineated. The object of this study is to provide a polysiloxane which exhibits elastomeric properties and is thermally stable as a result of co-hydrolysis condensation of methylvinylchlorosilane and dimethyldichlorosilane at ambient temperature followed by acid-catalyzed equilibrium copolymerization. Precise attention was placed on the synthesis of these polymers and effects of the structure on their thermal properties. The thermal stability and degradation mechanism of these

methyl vinyl siloxanes have also been determined by TGA and FTIR.

## II. Experimental

### A. Chemicals and reagents

Methylvinylchlorosilane  $[(CH_3)(CH_2=CH)SiCl_2]$ , Dimethyldichlorosilane  $[(CH_3)_2SiCl_2]$  and Trimethylchlorosilane  $[(CH_3)_3SiCl]$  were purchased from Sigma Aldrich Chemical and was used as received. Anhydrous sodium Sulphate ( $Na_2SO_4$ ) and Sulphuric acid ( $H_2SO_4$ ) were analytical reagent grade materials received from HmbG Chemical, used without purification.

### B. Synthesis of Methyl Vinyl Polysiloxane

250ml distilled water was placed in a 500ml conical flask equipped with three necked flask, dropping funnel and magnetic stirrer. The mixture of 99.63g (777.97mmol) dimethyldichlorosilane  $(CH_3)_2SiCl_2$ , 9.68g (68.62mmol) methylvinylchlorosilane  $(CH_3)(CH_2=CH)SiCl_2$  and 4.82g (44.37mmol) of trimethylchlorosilane  $(CH_3)_3SiCl$  were added dropwise into the water for over 3hrs. After the addition, the reaction mixtures were kept stirred for 2hrs at room temperature and were transferred into a separating funnel, and 70ml of ether were added into the separating funnel. The aqueous phases were separated from the organic phase and wash with water to neutrality. The organic phases were dried with anhydrous sodium sulphate ( $Na_2SO_4$ ), filtered and the solvent removed by evaporation, 66.10g of colorless and transparent liquid (X) obtained.

Exactly 66.10g amount (7.24mmol) of X and 0.72g (7.34mmol) sulphuric acid was added into a three necked flask and stirred for about 3h at 30°C. Distilled water was added to the flask and stir for 30 min to decompose the sulphate. After removing the aqueous phase; the remaining organic phase were dissolved in 60ml of ether. The organic phase were washed to neutrality with deionized water until litmus tests indicated the mixture was neutral and then dried with anhydrous  $Na_2SO_4$ . After the ether might have distilled off, the low-boiling point component was removed by vacuum distillation under 5mmHg at 120°C [2]. A faint yellow oil obtained at 58.12% yield.

### C. Characterization

Fourier transform infrared spectroscopy (FTIR) spectra were obtained using a Perkin-Elmer 782 Fourier transform infrared spectrometer at spectra range 4000-400 $cm^{-1}$  with a scan resolution of 4 $cm^{-1}$ . The thermal stability of the sample were analyzed using a SDT Q500 TA Instruments, with nitrogen as purge gas at a flow rate of 100 ml/min in order to decouple the thermal and thermo-oxidative degradation behavior of the sample. Samples were heated from 20°C to 500°C at a rate of 10°C/ min in platinum pans.

## III. Results and discussion

A series of polysiloxanes with controlled numbers of pendent vinyl groups were prepared. Polymethylvinylsiloxane homopolymers were synthesized via an acid- catalyzed redistribution reaction and terminated with a vinyl functional endcapping reagent (Figure 1). Sensitive functional groups like Si-H groups which are likely to be affected by basic catalysts are overcome by the use of acidic catalyst. Lewis acids and protonic acids such as  $H_2SO_4$ ,  $HClO_4$  and trifluoroacetic acid are variety of acidic catalyst reported [6]. Si-O bond is one of the most thermally stable bonds formed by silicon with bond dissociation energy of 110kcal/mol compare to Si-C bonds with 76kcal/mol [5]. This can most likely be explained by the different polarity of Si-O and Si-C bonds. The electronegativity's of Si, C and O are 1.8, 2.5 and 3.5, respectively, and both Si-C and Si-O bonds have the polarity, both bonds may be cleaved when attacked by electrophilic reagents. Since the polarity of the Si-O bond is higher than that of the Si-C bond, the Si-O bond is easier to cleave than the Si-C bond [5,9].

In the experiments, higher yields of PMVS were obtained, when ether was used as organic solvent than washing with water directly in the process of washing catalyst ( $H_2SO_4$ ) and its also prevent the formation of an emulsion.

The infrared absorption bands have been useful for determining the mode of coordination of the functional groups attached to the polysiloxanes backbone. One of the most notable features of the IR spectra of PMVS shown in Figure 2, is a very intense broad band around 1060 $cm^{-1}$  and 1020 $cm^{-1}$  were assigned to the asymmetric Si-O-Si stretching of a siloxane [7,13]. The band around 1598  $cm^{-1}$  was associated with vinyl groups [7]. The spectrum also shows three intensive vibrations corresponding to Si-CH<sub>3</sub> bonds: 2962 $cm^{-1}$ , 1258 $cm^{-1}$  and 791 $cm^{-1}$  due to symmetric CH<sub>3</sub> bending [6,13]. Lastly, the band at 3056 $cm^{-1}$  was

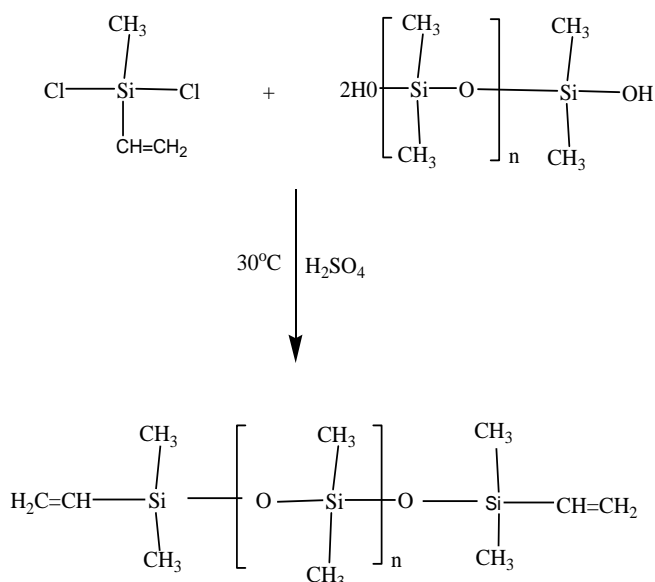


Figure 1: Synthesis route of polysiloxane containing methyl vinyl compound.

assigned to =CH stretching and C-H deformation bands at 841 and 752cm<sup>-1</sup>, with a weak band at 687cm<sup>-1</sup> [6,9].



Figure 2: FTIR Spectra of PMVS

The thermal stability and decomposition trails for PMVS were studied by TGA under air and nitrogen as purge gas. The TGA curves shown in Figure 3, point out the presence of three different stages of weight losses. The first stage was a prompt weight loss process start at roughly between the temperature range 50–125°C (accumulate about 22.37%), was linked with evaporation of solvent, precisely ethanol and/or water [7]. Exceeding this temperature, a second degradation was discovered with weight loss of 26.26% between the range 125-168°C, which can be related to random scissions within the polymer chains [8]. The final held from 170-500°C showing 45.66% weight losses, this could be associated to the dehydration of vinyl groups present in the SiO<sub>2</sub> [7,9].

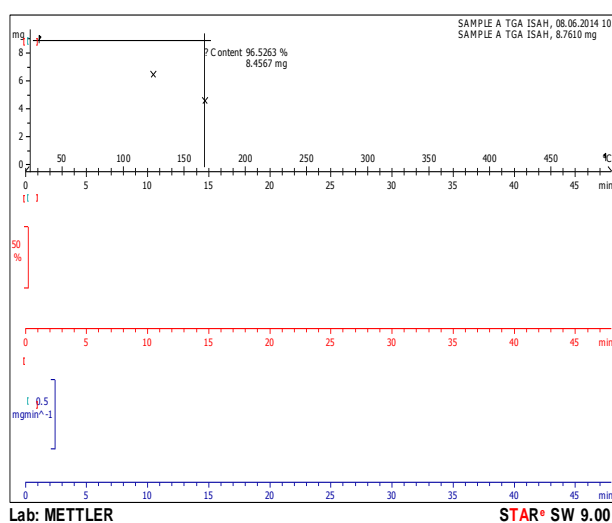


Figure 3: TGA Curve of PMVS

#### IV. Conclusions

Ambient-crosslinking polysiloxane compound were prepared by pre-hydrolysis/condensation of methylvinylchlorosilane (MVDCS) and dimethyldichlorosilane (DMDCS) followed by catalysis equilibrium copolymerization by sulphuric acid (H<sub>2</sub>SO<sub>4</sub>). The structure of PMVS has been confirmed by FTIR and TGA. The polymers showed high thermal decomposition temperatures and low residue yields at 500°C in a nitrogen atmosphere. The first one noticeable below 125°C was due to the evaporation of ethanol and water. The second one produced between 125°C and 168°C, was recognized to scissions within polymer chains or to volatile compounds formed during condensation reactions between Si-OH and Si-OR (R: CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub>) mixtures. The third loss was linked to the dehydration of silanol groups, or to the oxidation or degradation of methyl/vinyl groups.

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#### REFERENCES

- [1] F. Sun, and S. L. Jiang, (2007). Synthesis and characterization of photosensitive polysiloxane. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 254(1), 125–130.
- [2] C. Xu, and S. Feng, (2001). Synthesis and characterization of polysiloxane containing phenylethynyl groups. *Reactive and Functional Polymers*, 47(2), 141–146.
- [3] Y. Meng, (2012). Structure, morphology, and mechanical properties of polysiloxane elastomer composites prepared by in situ polymerization of zinc dimethacrylate. *Express Polymer Letters*, 6(11), 882–894.
- [4] X. Lan, W. Huang, and Y. Yu, (2010). Synthesis, characterization and properties of the polysiloxane-based episulfide resin. *European Polymer Journal*, 46(7), 1545–1556.
- [5] M.A. Brook, *Silicon in Organic, Organometallic, and Polymer Chemistry*. New York: John Wiley & Sons, Inc. 2000, pp. 381–441.
- [6] C. Bi, Z. Xiaoli, Y. I. Lingmin, and C. Fengqiu, (2007). Cationic Ring Opening Polymerization of Octamethylcyclotetrasiloxane Initiated by Acid Treated Bentonite. *Chin. J. Chem. Eng.*, 15(20576117), 661–665.
- [7] M. Criado, I. Sobrados, & J. Sanz, (2014). Polymerization of hybrid organic–inorganic materials from several silicon compounds followed by TGA/DTA, FTIR and NMR techniques. *Progress in Organic Coatings*, 77(4), 880–891.
- [8] P. Hammer, F.C.Dos Santos, B.M.Cerrutti, S.H. Pulcinelli, and C.V. Santilli, (2012). Highly corrosion resistant siloxane-polymethyl methacrylate hybrid coatings. *Journal of sol-gel science and technology*, 63(2), 266–274.
- [9] S. Jiang, B. Yu, K. Zhou, H. Yang, Y. Shi, S. Lo, and Z. Gui, (2014). Sol-gel synthesis and enhanced properties of a novel transparent PMMA

- based organic-inorganic hybrid containing phosphorus, nitrogen and silicon. *Journal of Sol-Gel Science and Technology*, 69(2), 418-428.
- [10] H. Liu, Q. Zhu, L. Feng, B. Yao, and S. Feng, (2013). Synthesis, structural characterization and properties of a cubic octa-n-propylsilsesquioxane inorganic-organic hybrid material. *Journal of Molecular Structure*, 1032, 29-34.
- [11] H. J. Naghash, and R. Mohammadrahimpanah, (2011). Synthesis and characterization of new polysiloxane bearing vinylic function and its application for the preparation of poly (silicone-co-acrylate)/montmorillonite nanocomposite emulsion. *Progress in Organic Coatings*, 70(1), 32-38.
- [12] W. Zeng, D. Gui, J. Liu, (2011, August). Synthesis and characterization of liquid silicone rubber for LED packaging (ICEPT-HDP), 2011 12<sup>th</sup> International Conference on (pp. 1-3). IEEE.
- [13] Y. Zheng, Y. Tan, L. Dai, Z. Lv, X. Zhang, Z. Xie, and Z. Zhang, (2012). Synthesis, characterization, and thermal properties of new polysiloxanes containing 1,3-bis(silyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane. *Polymer Degradation and Stability*, 97(11), 2449-2459.