

Separation of Low Molecular Siloxanes for Electronic Application by Liquid-Liquid Extraction

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Abstract—Silicone resins are widely used for electronic packaging as potting and encapsulating materials. Silicone resins have many advantages for electronic packaging applications such as superior electrical properties, thermal stability, low water absorption, etc. Furthermore, silicone resins are not only used as protective materials for integrated circuit (IC) devices but also as conducting materials for interconnection. However, silicone resins have two big drawbacks: low adhesion strength and low molecular weight creep. A simple liquid-liquid extraction method has been developed to purify silicone resins, which will improve adhesion strength and eliminate low molecular weight creep. This paper describes the results of the liquid-liquid extraction method to remove low molecular weight cyclic siloxanes. Fourier transform-infrared (FT-IR) spectroscopy was used to monitor the removal rate of low molecular weight cyclic siloxanes. Thermogravimetric analysis (TGA) was used to evaluate the purity of silicone resin. Gas chromatography-mass spectrometry (GC/MS) was used to identify the low molecular weight cyclic siloxanes. Thermomechanical analyzer (TMA), dynamic mechanical analyzer (DMA), and die shear test were used for evaluate the properties of silicone resin.

Index Terms— Adhesion, extraction, FT-IR, GC/MS, low-molecular weight creep, silicones.

I. INTRODUCTION

SILICONE resins have many properties that make them desirable for use in electronic packaging applications. These properties include flexibility, stress relief, thermal stability, moisture resistance, low ionic impurity levels, high permeability to gases, and good electrical performance. Thus, silicone resins are widely used in electronic packaging. For example, silicone resins have been utilized for IC packaging [1], [2] and silver filled silicone-based as conductive adhesives [3], [4]. Tessera's μ BGATM chip scale package uses a silicone elastomer as stress-relief buffer layer in the flexible circuit. Furthermore, silicone elastomer is the key encapsulant for environmental reliability testing [5].

However, there are two major drawbacks associated with silicone resins:

- 1) low adhesion strength;
- 2) low molecular weight creep.

Manuscript received March 17, 1999; revised November 4, 1999. This work was presented at the International Symposium on Advanced Packaging Materials, Braselton, GA, March 14–17, 1999.

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Publisher Item Identifier S 1521-334X(99)10395-1.

Low molecular weight creep is especially a problem because it causes contamination of devices and bond pad surfaces. These impurities are normally separated by fractional distillation. However, most cyclic siloxanes have high boiling points (>200 °C), and as such, the separation of low molecular weight cyclic siloxanes on a commercial scale is expensive.

The objective of this work is to remove low molecular weight cyclic siloxanes (Hexamethylcyclotrisiloxane, D₃; Octamethylcyclotetrasiloxane, D₄; Decamethylcyclopentasiloxane, D₅; etc.) from base silicone resins using cost effective liquid-liquid extraction.

II. EXPERIMENTAL

A. Materials

Dow Corning Corp. SYLGARDTM 527 primerless silicone dielectric gel Part A and Part B were used in this study. Polymethylhydrosiloxane from Petrarch Systems Co. was used as a hardener. Acetone (high-pressure liquid chromatography (HPLC) grade), D₃, D₄, and D₅ were purchased from Aldrich Chemical Company and used without further purification.

B. Extraction

First, 5.0 g of SYLGARD 527 Part A and Part B were each mixed with 10 g of acetone in a bottle. Then the samples were shaken by hand for a few minutes. Next, the samples were placed stationary with no vibration for separation. The extraction process was repeated up to six times.

C. TGA Sample Preparation

The extracted silicone resin Part A and Part B were mixed in a 1:1 by weight ratio. To this mixture, a trace amounts of polymethylhydrosiloxane (0.005 g/1g) was added. A control sample with no additive and no additive was also studied. These silicone resins were cured at 150 °C for 30 min and were measured by TGA (Model 2050 by TA Instruments).

D. Instrumentation

FT-IR was used to monitor the removal rate of low molecular weight cyclic siloxanes. These spectra were collected with a Nicolet 205 spectrometer. TGA was used to evaluate the purity of silicone resin. The weight loss curves were collected with TA Instruments Model 2050 Thermogravimetric

TABLE I
SOLVENT MISCIBILITY WITH SILICONE RESIN

Immiscible	Partly miscible	Miscible
Methanol	Acetone	Chloroform
Ethylene glycol	Dioxane	Toluene
Acetonitril	Ethanol	Hexane
Water	Isopropanol	Methylethylketone

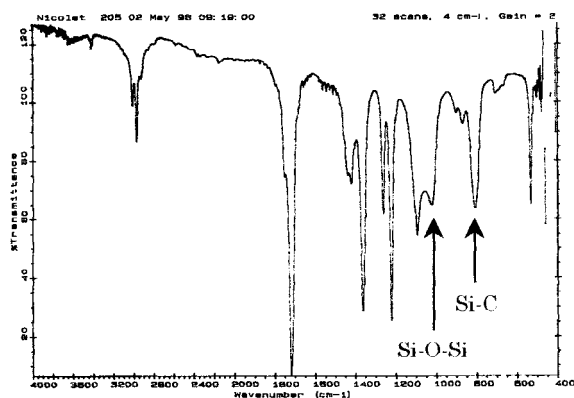


Fig. 1. FT-IR spectra of the solvent extract.

Analysis. Temperature was raised from room temperature to 200 °C at a rate of 5 °C/min. Isothermal measurements were performed at 200 °C for 120 min. Nitrogen was used as the purge gas. GC/MS was used to identify the low molecular weight cyclic siloxanes. These GC/MS spectra were measured with a Perkin Elmer AutoSystem XL Gas Chromatograph and TurboMass Mass Spectrometer.

III. RESULTS AND DISCUSSION

A. Solvent Selection

The first step in the extraction process was to add an immiscible or partly miscible solvent to the silicone resin. The solvents used in this study are shown in Table I. Among these solvents, acetone is the one that easily dissolves low molecular weight cyclic siloxanes while remaining partly miscible with the base silicone resin. Therefore, acetone was selected and used for the extraction solvent in this research.

B. FT-IR Study

FT-IR spectra of the first time extracted solvent is shown in Fig. 1. Strong absorption peaks at 1000 to 1100 cm^{-1} and at 800 cm^{-1} were observed in the extracted solvent. The silicone had an absorption at 1000 cm^{-1} , which is characteristic of Si-O-Si antisymmetric stretch absorption. Also, the silicone had an absorption at 800 cm^{-1} , which is characteristic of Si-C symmetric stretch absorption [6]. These results show that low molecular weight siloxanes can be extracted using acetone.

Table II shows the concentration of low molecular siloxanes after each extraction. After four to five extractions, there were very small peaks at 800 cm^{-1} . The heights of these peaks are the same as pure acetone's peak height. Therefore, low molecular siloxanes can be removed by liquid-liquid extraction repeated four to five times using acetone.

TABLE II
THE CONCENTRATION OF EXTRACTED LOW MOLECULAR SILOXANES (wt%)

Extraction No.	Part A	Part B
1st	5.0	3.0
2nd	1.2	1.5
3rd	1.5	1.2
4th	<1.0	<1.0
5th	<1.0	<1.0

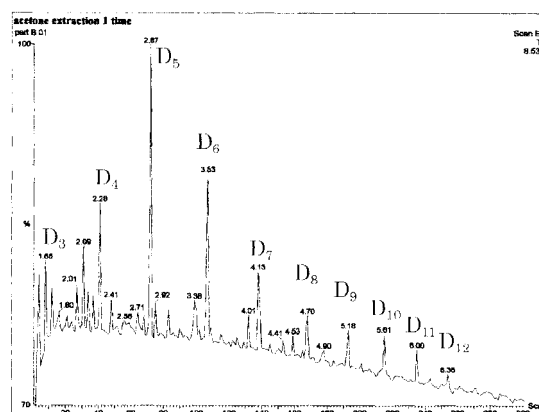


Fig. 2. GC chart of first extraction.

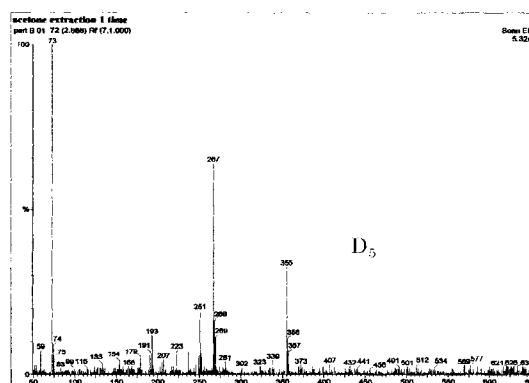


Fig. 3. MS spectra of D₅.

C. GC/MS Study

1) *Qualitative Analysis:* Solvents which were used to perform the extractions with silicone resin were analyzed using gas chromatography-mass spectrometry (GC/MS). This technique separates the low molecular weight cyclic siloxanes and further provides a mass spectrum of each component. Fig. 2 shows the GC chart of the solvent after the first extraction. D₃ to D₁₂ were detected by GC and this result shows clearly that low molecular siloxanes can be extracted. Many small peaks were also observed among the low molecular weight cyclic siloxanes' peaks. These peaks were determined to be vinyl terminated siloxanes and silicone-hydrides by MS analysis. These data show that the liquid-liquid extraction can remove not only low molecular weight cyclic siloxane but also other low molecular weight siloxanes.

Fig. 3 shows a MS spectra of D₅. All of the spectra show a common fragmentation pattern. The most noticeable fragmentation is the facile loss of one CH₃ group leading to a

TABLE III
PEAK ASSIGNMENTS FOR GC-MS SPECTRA OF THE CYCLIC SILOXANES

m/z	Composition	Species
59	SiC ₂ H ₇	SiH(CH ₃) ₂ ⁺
73	SiC ₃ H ₉	Si(CH ₃) ₃ ⁺
73	SiOC ₂ H ₅	$\left(\left[\begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}-\text{O}- \\ \\ \text{CH}_3 \end{array} \right] - \text{H} \right)^+$
193	Si ₃ O ₄ C ₃ H ₉	(D ₄ -CH ₃ -Si(CH ₃) ₄) ⁺
251	Si ₃ O ₃ C ₅ H ₁₅	(D ₅ -CD ₃ -(OSi(CH ₃) ₄)) ⁺
267	Si ₄ O ₅ C ₅ H ₁₅	(D ₅ -CH ₃ -Si(CH ₃) ₄) ⁺
355	Si ₅ O ₅ C ₉ H ₂₇	(D ₅ -CH ₃) ⁺

TABLE IV
EXTRACTION EVALUATION OF SILICONE RESIN (UNIT: wt%)

Extraction	GC-MS results*	FT-IR results
1st	0.217	3.5
2nd	0.135	1.2-1.5
3rd	0.017	1.2
4th	<0.001	<1.0

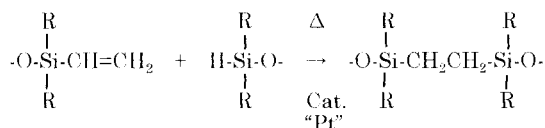


Fig. 4. Heat curable silicone resin cure mechanism.

(M-CH₃)⁺ ion in all cases. Another common loss corresponds to the loss of Si(CH₃)₄ from the cyclic (M-CH₃)⁺ species and this fragmentation has been accounted for previously in terms of a rearrangement of the cyclic siloxane [7], [8]. A table of the common peaks observed in the MS spectra is given in Table III.

2) *Quantitative analysis of Extracts:* The concentration change of D₅ is shown in Table IV. The concentration of D₅ after four extractions becomes less than 0.001 wt%. The FT-IR results and GC/MS results show the same trend. The difference in concentration between GC/MS and FT-IR is because FT-IR results are the sum of D₃ to D₁₂ and other low molecular siloxanes.

D. TGA Study

Most silicone resin chemistry is based on the hydrosilylation addition reaction of silicone-vinyl and silicone-hydride as shown on Fig. 4 [9].

The low molecular weight cyclic siloxanes and silicone-hydride were removed simultaneously by extraction which was discussed in the GC/MS study. Therefore, the silicone resin was mixed with silicone-hydride in a 1:0.005 ratio and cured at 150 °C for 30 min.

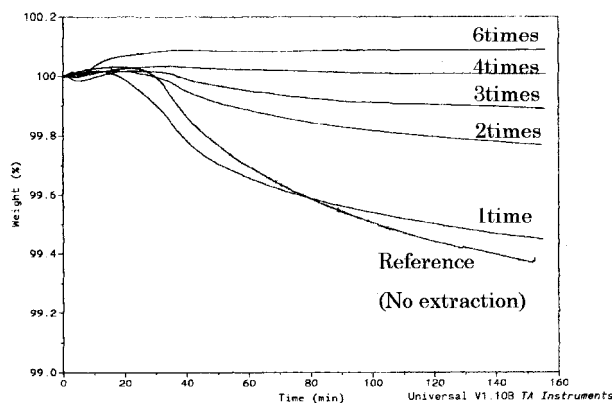


Fig. 5. TGA of varied number of extractions were performed cured silicone.

Fig. 5 shows several extraction conditions' weight loss curves of cured silicone resin in TGA analysis. The reference (no extraction) is also shown in Fig. 5. The weight loss of the reference silicone was about 0.6%. After one extraction, the sample's weight loss was about 0.3%. After two and three extractions, the samples' weight losses were less than 0.1%. These results were much smaller values than those obtained by Suzuki and colleagues [10]. The weight loss of samples on which the extractions were performed more than 4 times were very stable during the TGA isothermal measurement at 200 °C. These results show that the low molecular volatile siloxane was removed from the silicone resin.

IV. CONCLUSION

It has been shown that the liquid-liquid extraction using acetone can be used to remove low molecular weight cyclic siloxanes from base silicone resin. However, low molecular silicone-hydride and low molecular vinyl modified siloxane were also extracted simultaneously from the base silicone resin. FT-IR, TGA, and GC/MS were used for the analyzes of extracted low molecular siloxanes.

FT-IR, TGA, and GC/MS data were in good agreement with low molecular weight cyclic siloxane removal.

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