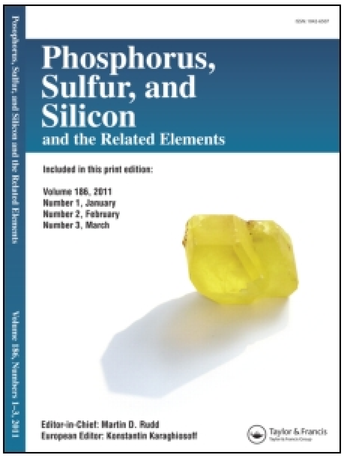

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Yang, Xiong-fa , Dong, Hong , Wu, Chuan and Jiang, Jian-xiong(2009) 'Synthesis and Characterization of Ethylhydrosilicone Fluids as Liquid Cross-Linking Agents for the Encapsulant of Light Emitting Diodes', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 11, 2870 — 2876

To link to this Article: DOI: 10.1080/10426500802591366

URL: http://dx.doi.org/10.1080/10426500802591366

Phosphorus, Sulfur, and Silicon, 184:2870–2876, 2009
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802591366

Synthesis and Characterization of Ethylhydrosilicone Fluids as Liquid Cross-Linking Agents for the Encapsulant of Light Emitting Diodes

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We report a series of ethylhydrosilicone fluids synthesized through the ring-opening copolymerization of mixed cyclosiloxanes and end-capped with the 1,1,3,3-tetramethyl-1,3-dihydrosiloxane using anionic exchange resin as catalyst. The mixed cyclosiloxanes consisted of methylphenylcyclosiloxane ($D_n^{Me,Ph}$, $n = 3$, 4), tetramethylhydrogencyclosiloxane (D_4^{H}), and tetramethylethylcyclosiloxane ($D_4^{Me,Et}$). The refractive indices of the obtained silicone fluids were determined, and these products were further characterized by SEC, ^{1}H NMR, TGA, and DSC. The DSC results indicated that the cold resistance of the silicone fluids obtained was improved with the increase of (MeEtSiO) unit content. Therefore, the silicone fluids with good cold resistance can be used as liquid cross-linking agents for LED encapsulants to enhance the cold tolerance of LED devices.

Keywords Cross-linking agent; encapsulant material; ethylhydrosilicone fluid; light emitting diode (LED)

INTRODUCTION

A light emitting diode (LED) is a type of semiconductor lighting device. Compared with traditional filament-based lighting devices, an LED exhibits various advantages, such as longer life, lower power requirements, better initial drive characteristics, higher resistance to vibration, and higher tolerance to repeated power switching. Because of these favorable characteristics, LED is widely used in such applications as indicators and lower power lighting sources. With the rapid

Received 11 July 2008; accepted 28 October 2008.

This work was created with the financial support of the National High-Tech Research and Development Plan of China (Grant No. 2006AA03A134 and No. 2006AA050203-1) and Zhejiang Provincial Natural Science Foundation of China (Grant No. Y4080264).

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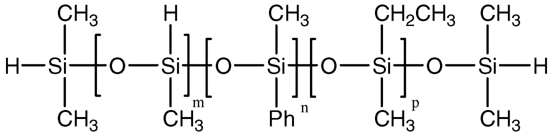
development of power-type LED, it may be used as a fourth generation light source in the near future.[1]

The packaged LED light source includes a LED die and a kind of light-transmissive material that encapsulates the LED die. Generally, epoxy resins are good and cheap sealing materials for LED devices with lower power. While for a white LED with higher power, some problems such as UV-induced yellowing of epoxy resin encapsulants, and cracking of encapsulants induced by heat generation resulting from size reduction of LED parts are serious,[2–5] and will shorten the service deadline of LED devices. Therefore, overcoming these problems is urgently needed, and silicone materials are selected as the ideal encapsulant materials because of their important properties, especially their excellent thermal and UV resistance.

Silicone polymers can be cured by different mechanisms, but for an LED encapsulant, polymers cured by hydrosilylation catalyzed by platinum and its various complexes are mostly preferred. Although commercially purchased transparent and colorless hydrogen-containing silicone fluids may function as cross-linking agents, their refractive index at 25°C is lower than 1.5, which lowers the light extraction efficiency of an LED package and so cannot be used in an LED encapsulant. Hydrogen-containing silicone fluids with higher refractive indices serving as the cross-linking agents for LED encapasulants can be prepared by co-hydrolysis and condensation of one or more chlorosilanes with hydrochlorosilane, and a phenyl group is especially desirable.[6–13] However, this process is uncontrollable, and it generates considerable waste water containing HCl. Moreover, the composition of the silicone fluids obtained is complicated and doped with homo- and copolymers, which will lower the transmittance of cross-linking agents.

With the widespread use of LEDs in severe cold regions, LED encapsulants with good cold tolerance will be absolutely necessary. Polysiloxanes with ethylsilyl group have good cold tolerance[14]; therefore, ethylsilyl is introduced into the backbone of cross-linking agents.

Here we provide an environmentally friendly method to produce silicone fluids containing both hydrosilyl and ethylsilyl groups (referred to as ethylhydrosilicone fluid in Scheme 1) that function as the cross-linking agents for LED encapsulant. Silicone fluids were prepared by the ring-opening copolymerization of mixed cyclosiloxanes including D_4^{H}, $D_n^{Me,Ph}$, and $D_4^{Me,Et}$, and end-capped with 1,1,3,3-tetra-methyl-1,3-dihydrosiloxane. The refractive indices of the silicone fluids obtained are measured, and these products are further characterized by SEC, ^{1}H-NMR, TGA, and DSC. Liquid cross-linking agents with good cold resistance are helpful to improve the cold resistance of the LED encapsulant materials.



SCHEME 1 The structure of the ethylhydrosilicone fluids as liquid cross-linking agents for light emitting diode encapsulants.

RESULTS AND DISCUSSION

The influence of the feeding molar ratio of the (MeEtSiO) unit was investigated and is summarized in Table I. It can be seen that the molar ratio of ethyl group bonded to the silicone center in silicone fluids increased with the increase of the feeding molar ratio of the (MeEtSiO) unit. However, the feeding molar ratio of the (MeEtSiO) unit has almost no influence on the refractive index, molecular weight, or the content of the —Si—H in the products.

The ^{1}H NMR spectra of the silicon fluids obtained are presented in Figure 1. The signals of the phenyl group bonded to the silicone center could be clearly identified at 7.20∼7.80 ppm. The chemical shifts at 0∼0.65 ppm were assigned to the $-CH_3$ bonded to the silicone center. The characteristic signals located at 0.80∼0.94 ppm and 4.80∼4.95 ppm in the ^{1}H NMR spectra could be attributed to the proton of the $-CH_2-$ in the ethyl group bonded to the silicone center and the —Si—H group, respectively. It could be further determined from Figure 1 that peak

TABLE I The Influence of $D_4^{Me,Et}$ Feeding Molar Ratio on Silicone Fluids

Entry	(MeEtSiO)/((MeHSiO) + (MePhSiO)) (mol %)	Refractive index	Mn (10^4)	Et/Si (%)	Ph/Si (%)	H/Mn^{NMR} (%)
1	0	1.5230	0.83	0	65.8	0.287
2	1	1.5130	0.75	1.59	57.1	0.294
3	3	1.5154	0.77	3.45	57.5	0.270
4	5	1.5150	0.83	5.86	58.2	0.257
5	7	1.5145	0.83	7.90	57.3	0.253

Conditions: 65°C, (MeHSiO)/((MeHSiO) + (MePhSiO)) = 35:100, 8.4 g D_4^H, 35.4 g $D_n^{Me,Ph}$, 0.67 g 1,1,3,3-tetra-methyl-1,3-dihydrogensiloxane, 2.19 g anionic exchange resin.

$H/M_n^{NMR} = 30 \times I_{Si\text{-}H}/(1590 \times I_{Si\text{-}H} + 732 \times I_{Ph} + 1215 \times I_{Si\text{-}CH2} + 70 \times I_{CH3}) \times 100\%$

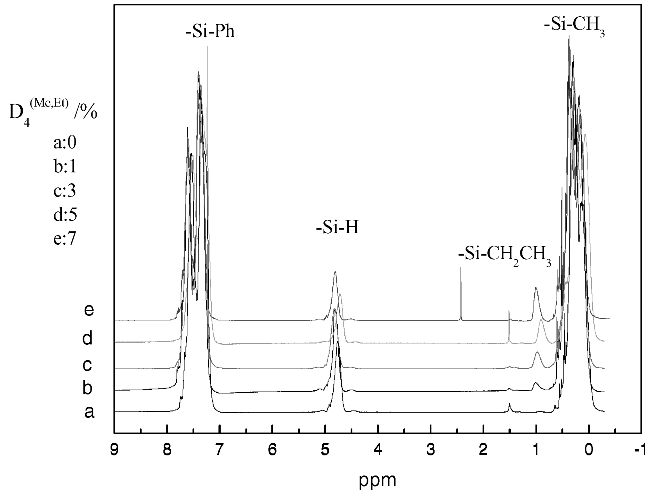


FIGURE 1 The ^{1}H NMR spectra of the ethylhydrosilicone fluids.

intensity of the ethyl group (0.80~0.94 ppm), viz. the integration of the proton of the $-CH_2-$ in the ethyl group, increased with the increase of the feeding molar ratio of the (MeEtSiO) unit.

The intensive degradation temperature is a criterion of heat stability of polymers. The TGA results for thermal degradation of the ethylhydrosilicone fluid are plotted in Figure 2 and Table II. The heating

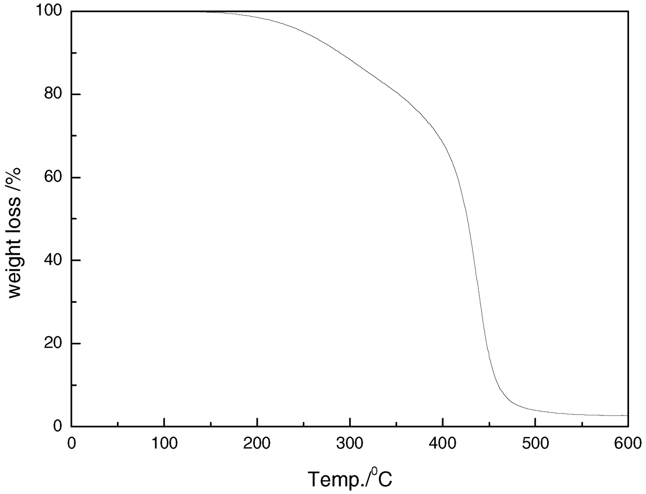


FIGURE 2 The TGA curve of the ethylhydrosilicone fluid (Table I, entry 4).

TABLE II Thermal Properties of the Ethylhydrosilicone Fluid (Table I, entry 4)

Weight loss (%)	1	3	5	10
Temp.(°C)	194.4	231.4	253.4	287.4

rate was 10°C/min. Only when the temperature was higher than about 250°C did the silicone fluid begin to obviously degrade; therefore, the silicone fluids exhibit good heat stability.

The DSC curves of silicone fluids with different (MeEtSiO) content are displayed in Figure 3. All samples are initially heated to 100°C and held for 2 min to erase the thermal history, then cooled to –100°C at a cooling rate of 10°C/min, and finally heated to 150°C again at a rate of 10°C/min. For comparison, the DSC curve of silicone fluid not containing a (MeEtSiO) unit is also given. Figure 3 shows the second heating cycle of the fluid samples. Single T_g values are obtained for all fluids, and T_g values regularly decreased with an increase of the (MeEtSiO) unit content in the copolymers, which suggests that the cold resistance of silicone fluids was improved with the increase of the (MeEtSiO) unit content.

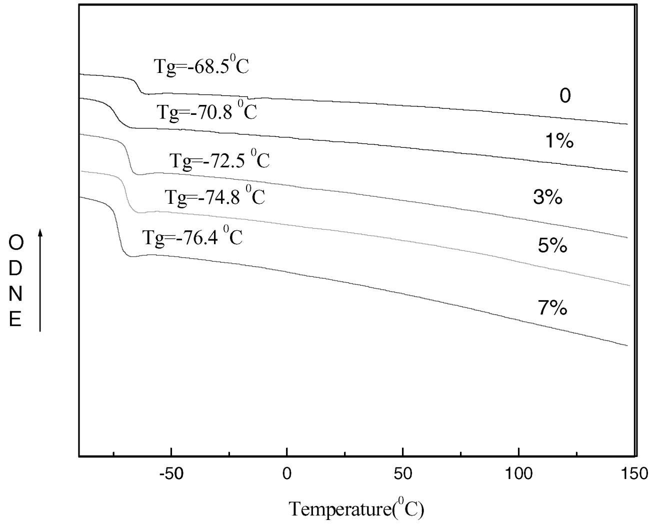


FIGURE 3 DSC curves of the ethylhydrosilicone fluids.

CONCLUSIONS

A series of ethylhydrosilicone fluids with good cold resistance have been prepared by an environmentally friendly method. The DSC characterization of the silicone fluids obtained indicated that the cold resistibility of the silicone fluids was improved with the increase of the (MeEtSiO) unit content, and the silicone fluids can be used as liquid cross-linking agents for the LED encapsulant to provide an LED with excellent cold resistance properties.

EXPERIMENTAL

General Process for the Polymerization

All polymerizations were performed in a 250-mL three-necked flask under argon atmosphere. 8.4 g D_4^H (Acros), 35.4 g $D_n^{Me,Ph}$ (Acros) and the appropriate amount of $D_4^{Me,Et}$(Acros) were added into the three-necked flask and dehydrated under 40°C/–0.096 MPa. Then 0.67 g of 1,1,3,3-tetra- methyl-1,3-dihydrosiloxane and 2.24 g of cationic exchange resin were added. The mixture was heated to 65°C and polymerized for 5 h. The catalyst was separated by filtration with Nutsche filters. The liquid was collected, taken off low-boiling residues under 205°C/–0.096 MPa for 2 h, then cooled down to room temperature, and the product is obtained.

Measurements

The refractive index was measured on an Abbe-refrector at 25°C. The number-average molecular weight (M_n) and molecular weight distribution (MWD) were determined in toluene at 25°C with polystyrene as a standard by a Waters 150°C size exclusion chromatograph (SEC). Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer in $CDCl_3$ at 25°C with TMS as an internal reference. Thermogravimetric analysis (TGA) tests were conducted by a TG 209C instrument with a heating rate of 10°C/min under a N_2 atmosphere with a carrier gas flow rate of 20 mL/min. Differential scanning calorimetric (DSC) curves were recorded on a DSC Q100 apparatus under the N_2 atmosphere with a carrier gas flow rate of 20 mL/min. The samples were heated to 150°C, held for 2 min to erase the thermal history, then cooled to –100°C at a rate of 10°C/min, and finally heated to 150°C at a heating rate of 10°C/min again.

REFERENCES

[1] J. T. Barnett and P. S. Tillinghast, High power light emitting diode, Eur. Pat. 1467416 (2004); *Chem. Abstr.*, **141,** 304108 (2004).

[2] S. Yoshinori, S. Kensho, N. Yasunobu, and M. Toshio, Light emitting device and display device, WO Pat. 9805078A1 (1998); *Chem. Abstr.*, **128,** 160811 (1998).

[3] S. Yoshinori, S. Kensho, N. Yasunobu, and M. Toshio, Light emitting device, Eur. Pat. 1271664 A2 (2003); *Chem. Abstr.*, **138,** 80440 (2003).

[4] S. Yoshinori, S. Kensho, N. Yasunobu, and M. Toshio, Light emitting device and display, Eur. Pat. 1017112 (2000); *Chem. Abstr.*, **133,** 96587 (2000).

[5] K. Miyoshi, Silicone resin composition for LED devices, Eur. Pat. 1 424 363 A1 (2004); *Chem. Abstr.*, **141,** 8267 (2004).

[6] T. Goto, E. Tabei, and A. Yamamoto. Curable silicone resin composition, Janan Pat. 20030919 (2003); *Chem. Abstr.*, **142,** 337399 (2003).

[7] K. Nakazawa and I. Tsukuba, Encapsulating composition for LED, WO Pat. 107458A2 (2004); *Chem. Abstr.*, **142,** 45677 (2004).

[8] T. Kashiwagi and T. Shiobara, Light-emitting semiconductor embedding/protecting material and light-emitting semiconductor device, US Pat. 0006794 A1 (2005); *Chem. Abstr.*, **142,** 135631 (2005).

[9] T. Shiobara, T. Kashiwagi, and K. Imazawa, Silicone resin lens for light-emitting diode, and manufacturing method, Japan Pat. 324596 (2006); *Chem. Abstr.*, **145,** 513632 (2006).

[10] E. Tabei and A. Yamamoto, Curable silicone resin composition, Japan Pat, 293524 (2003); *Chem. Abstr.*, **142,** 219761 (2003).

[11] J. V. Crivello, Silicone encapsulants for light emitting diodes, US Pat. 0134440 (2006); *Chem. Abstr.*, **144,** 433705 (2006).

[12] L. D. Boardman, D. S. Thompson, C. A. Leatherdale, and A. J. Ouderkirk, Method of making light emitting device with silicon-containing encapsulant, US Pat. 0252336 (2005); *Chem. Abstr.*, **146,** 451312 (2005).

[13] M. Yoshitsugu, K. Tomoko, T. Atsushi, and E. Hiroji, Curable organopolysiloxane composition and a semiconductor device made with the use of this composition, WO Pat. 037927 (2004); *Chem. Abstr.*, **140,** 391880 (2002).

[14] S. M. Xing and Y. L. Wang, *The Synthesis Process and Products Application of Silicone* (Chemical Industry Press, Beijing, 2000), p. 348.