

A Low Temperature Vulcanized Transparent Silane Modified Epoxy Resins for LED Filament Bulb Package

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Electronic Supplementary Information

Abstract In this work, low-temperature vulcanized, transparent silane modified epoxy resins for LED filament bulb package were prepared. Firstly, transparent silane modified epoxy resins were produced through a controllable sol-gel method using γ -(2,3-epoxypropoxy)propyltrimethoxysilane and dimethyldiethoxysilane. The features of the reaction were investigated and the products were characterized in detail. Subsequently, various curing agents were explored to prepare transparent silane modified epoxy resins. The silane modified epoxy resins cured by PEA-230 at a fairly low temperature (40 °C/2 h then 60 °C/1 h) exhibited excellent thermal stability with a thermal degradation temperature as high as 316.5 °C and adjustable hardness between 40–60 shore A. The application tests showed the materials obtained were good candidates for LED filament bulb package.

Keywords Silane modified epoxy resins; LED filament bulb; Package materials

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INTRODUCTION

Recently, light emitting diodes (LEDs) have received considerable attention attributed to their excellent properties, such as energy saving, longer service life, environmental friendliness, higher luminosity at low currents and voltages, versatility with a variety of colours, higher resistance to vibration, and higher tolerance to repeated power switching^[1–4].

Packaging materials are crucial for LEDs. Epoxy resins have been used as LED packaging materials for several decades because of their superior properties such as low cost, efficiency, good transparency, high refractive index and good adhesion. However, due to an inherent brittle nature, poor stability against yellow light and poor crack resistance, epoxy resins are no longer ideal packaging materials for the high-power LEDs^[5–7]. Silicone resins have been most widely used in LED package owing to their outstanding properties including high thermal stability^[5], good transparency^[1–4], a wide range of service temperatures^[1, 2], minimal moisture absorption^[6, 8–10], low glass transition temperature^[11, 12], etc. However they have relatively poor mechanical strength and adhesive properties^[12, 13]. To improve the mechanical and adhesive properties of the silicone resins while retaining the

inherent properties of silicone moiety, several different approaches have been applied to prepare epoxy-modified silicone resin using the reaction of epoxy monomers with siloxanes having terminal hydroxy groups^[14–16], such as incompletely condensed silsesquioxanes, e.g. phenyltrisilanol polysilsesquioxane^[17]. Recently, a hyperbranched epoxy resin with a silicone skeleton was synthesized through a hydrosilylation reaction catalyzed by a heterogeneous halloysite-supported platinum catalyst^[18, 19].

The invention of LED filament bulbs (Fig. S1, in electronic supplementary information, ESI) with wide light distribution of 360° gives LED lighting new directions. In addition to the common requirements of traditional LED equipment, filament bulb packaging material should have appropriate viscosity, good thixotropy and be able to be cured at lower temperature to guarantee minimal changes in size and shape. Inspired by the interesting work mentioned above, in this work, a low temperature vulcanized, transparent, silane modified epoxy resins for LED filament bulb package is developed and the performances of the packaging material are investigated in detail.

EXPERIMENTAL

Materials

γ -(2,3-Epoxypropoxy)propyltrimethoxysilane (99.9%) and dimethyldiethoxysilane (99.9%) were obtained from Hubei Xinlantian Co., Ltd. (Xiantao, China) and Zhengbang

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Silicone Co., Ltd. (Quzhou China) respectively. Hexahydro-4-methylphthalic anhydride (4-MHHPAN, AR) was purchased from Chengdu Xiya Chemical Corporation (Chengdu, China). *N,N*-dimethylbenzylamine (AR) and polyoxypropylenediamine ($\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2[\text{OCH}_2\text{CH}(\text{CH}_3)]_n\text{NH}_2$) with average molecular weight of 230, 400 and 2000 (Abbreviated as PEA-230, PEA-400 and PEA-2000 respectively, AR) were bought from Beijing HWRK Chemical Co. (Beijing, China). The LED filament bulb chip was supplied by Zhejiang Z-Light Optoelectronics Co., Ltd. (Hangzhou, China).

General Procedure for the Synthesis of Silane Modified Epoxy Resins

Silane modified epoxy resins were synthesized by a sol-gel process with γ -(2,3-epoxypropoxy)propyltrimethoxysilane and dimethyldiethoxysilane according to Fig. 1. Specifically, an aqueous solution of 3.14 g of HCl (36.5%) and 50.0 g of deionized water was added dropwise into a three-neck flask containing γ -(2,3-epoxypropoxy)propyltrimethoxysilane (103.7 g, 0.439 mol), dimethyldiethoxysilane (53.2 g, 0.359 mol) and toluene (157.0 g), and stirred quickly over 4 h at 60 °C. Subsequently, the organic phase of the reaction mixture was washed with deionized water until the pH value reached 7. The solvent and the low-boiling residues in the organic phase were then removed at 140 °C/ 2.67×10^4 Pa, and a transparent liquid was produced.

Curing Procedure of the Silane Modified Epoxy Resins

The silane modified epoxy resins were cured with 4-MHHPAN accelerated by *N,N*-dimethylbenzylamine. The silane modified epoxy resins, 4-MHHPAN and *N,N*-dimethylbenzylamine were mixed according to the molar ratio of epoxy group:MHHPAN:*N,N*-dimethylbenzylamine = 100:85:2 and degassed under vacuum until no bubbles were observed, and finally the composite was cured at 80 °C for 1 h, 120 °C for 1 h and 150 °C for another 2 h.

The silane modified epoxy resins were alternatively cured with PEA. PEA and silane modified epoxy resins were mixed according to various *r* values (the molar ratio of active hydrogen to epoxy group) and degassed under vacuum until no bubbles were observed, and the composite was cured at 40 °C for 2 h and 60 °C for 1 h (as shown by Fig. S2, in ESI).

Characterization

^1H -NMR spectra were recorded on a Bruker AVANCE AV400 (400 MHz) spectrometer with CDCl_3 as the solvent at room temperature without tetramethylsilane (TMS) as internal reference. Fourier transform infrared (FTIR)

spectroscopic analysis was carried out using a Perkin-Elmer FTIR 2000 spectrometer over the wavenumber range 4000–400 cm^{-1} using KBr pellets. The epoxy value was measured by hydrochloric acid acetone titration according to “Determination of the epoxy value of plasticizers” (GB/T 1677-2008, Beijing, Chinese Standards Press, 2008). Transmittance spectra of silicone resin (placed in a 10 mm quartz absorption cell) from 200 nm to 800 nm were recorded on a Unico UV-4802 UV-Vis spectrophotometer (Unico Instrument Co. Ltd., Shanghai). The hardness of the cured samples was measured with an LX-A durometer (Zhenwei Testing Machinery Co. Ltd., Jiangdu, China) according to ASTM D 2240. Thermogravimetric (TG) analyses were performed using a TG 209C apparatus (Germany) at a rate of 10 $\text{K} \cdot \text{min}^{-1}$ in a nitrogen atmosphere from 25 °C to 800 °C. Differential scanning calorimetry (DSC) measurements were performed with a DSC Q100 (TA Instruments, American) apparatus under nitrogen atmosphere with a carrier gas flow rate of 20 $\text{mL} \cdot \text{min}^{-1}$. The samples were heated to 80 °C, held for 2 min to erase the thermal history, then cooled to –50 °C at a rate of 10 $\text{K} \cdot \text{min}^{-1}$, and finally heated again to 100 °C at a heating rate of 10 $\text{K} \cdot \text{min}^{-1}$. The apparent curing contents of the silane modified epoxy resins cured by PEA-230 with different *r* values were measured by Soxhlet extraction with toluene at 150 °C for 4 h. The tensile shear test was carried out according to GB/T 7124-2008. The yellowness index (YI) was calculated by equation $\text{YI} = (T_{680} - T_{420})/T_{560} \times 100\%$ according to ASTM E313-10^[20], where T_{420} , T_{560} and T_{680} were the transparency at the wavelength of 420, 560 and 680 nm, respectively. The package and the photoelectric properties measurement of LED filament bulb were carried out by Zhejiang Z-Light Optoelectronics Co. Ltd.

RESULTS AND DISCUSSION

Synthesis of the Silane Modified Epoxy Resins

γ -(2,3-Epoxypropoxy)propyltrimethoxysilane and dimethyldiethoxysilane were chosen as monomers to synthesize silane modified epoxy resins catalyzed by acid. HCl (36.5%) was explored as a catalyst for the sol-gel reaction and it proved to be a successful approach. The silane modified epoxy resins produced using HCl (36.5%) catalysis were all transparent, with fairly high yield and good storage stability. The effect of various R/Si on the silane modified epoxy resins was investigated and is listed in Table 1. Generally, the yield and epoxy value of the products declined steadily with the increase of R/Si. Table 1 shows that the epoxy values of the silicone resins obtained decreased with the

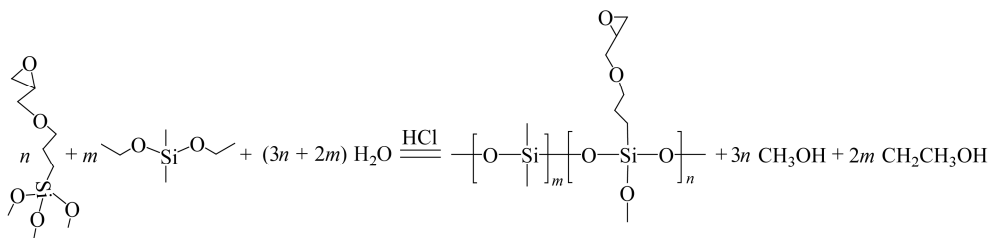


Fig. 1 Synthetic scheme for the silane modified epoxy resin

Table 1 Effects of various R/Si on the silane modified epoxy resins

Entry	R/Si designed by feed ratio	R/Si measured by $^1\text{H-NMR}$	Yield (%)	Epoxy value calculated by feed ratio	Epoxy value measured by titration ^a
1	1.45	1.45	62.2	0.43	0.26
2	1.50	1.46	52.6	0.41	0.25
3	1.60	1.64	45.0	0.36	0.24
4	1.70	1.72	46.5	0.29	0.17
5	1.80	1.85	27.5	0.21	0.10

^a Measured by hydrochloric acid acetone titration. The amount of HCl (36.5%) was 2% of the total mass of siloxanes. Toluene was used as solvent for the sol-gel reaction and the mass of toluene was equal to the total mass of siloxanes.

increment of the designed by feed ratio and it means that the molecular network structure of the products can be well controlled by controlling the feed molar ratio of monomers. It can also be seen from Table 1 that the epoxy values measured by titration were obviously smaller than those calculated by feed ratio, which might be attributed to the ring opening of epoxy group catalyzed by HCl during the course of the sol-gel reaction.

To identify the structure of the products obtained, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of the silane modified epoxy resins were obtained and are shown in Figs. 2 and 3

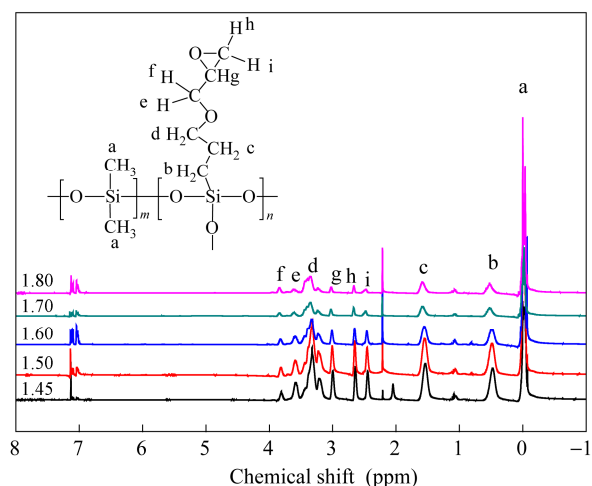


Fig. 2 $^1\text{H-NMR}$ spectra of the silane modified epoxy resins with various of R/Si

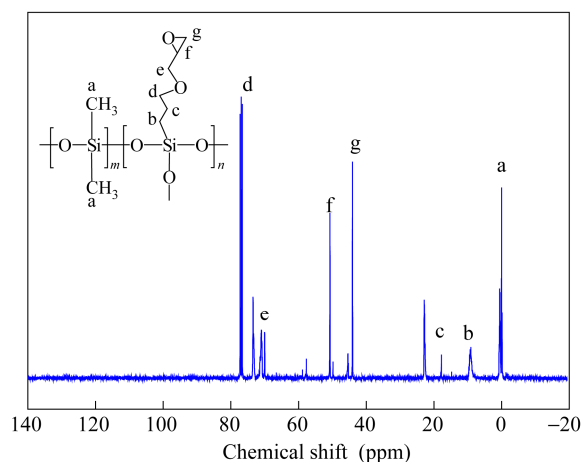


Fig. 3 $^{13}\text{C-NMR}$ spectrum of the silane modified epoxy resins with R/Si of 1.8

respectively. The signals of $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra are assigned as in Figs. 2 and 3, respectively, indicating that the products obtained were silane modified epoxy resins.

The Effects of Various Curing Agents on the Vulcanized Silane Modified Epoxy Resins

Significantly, the curing agents played an important role in producing transparent silane modified epoxy resins without turning yellow. In an attempt to prepare a transparent silane modified epoxy resins for an LED filament bulb package, firstly the synthesized silane modified epoxy resins were cured with 4-MHHPAN accelerated by *N,N*-dimethylbenzylamine as shown by Fig. 4(a). It can be seen from Fig. 4(a) that the cured materials became yellow if the cure temperatures reached 120 °C. In contrast, PEA can cure the silane modified epoxy resins at a fairly low temperature (40 °C for 2 h, 60 °C for 1 h) and Fig. 4(b) indicates that the cured materials all had very high transparency without yellowing. It might be attributed to the thermal stability of the product cured with PEA superior to that of the product cured with 4-MHHPAN, which can be seen by the TGA analysis shown in Fig. 5. Figure 5 exhibits that the thermal degradation temperature of cured products decreased with increasing molecular weight of PEA. It also shows that the thermal degradation temperature of silane modified epoxy resins cured with PEA-230 was as high as 316.5 °C, which is much higher than the thermal degradation temperature of the neat epoxy resin E20 cured by PEA-230^[21].



(a) Cured with MHHPAN accelerated by *N*-benzyl dimethylamine



(b) Cured by PEA-230 with $r = 1$

Fig. 4 The photos of the cured silane modified epoxy resins

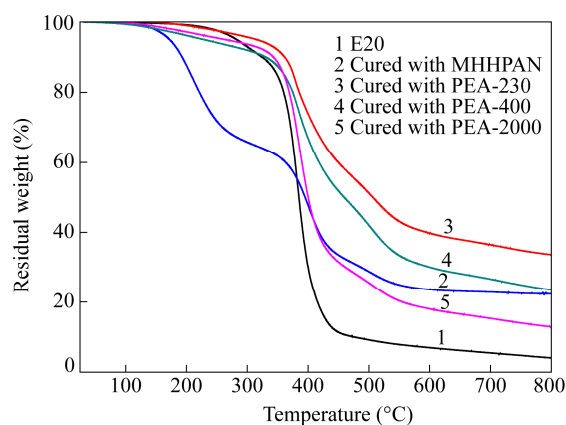


Fig. 5 The TGA curves of silane modified epoxy resin (entry 2 in Table 1) cured with various curing agents

The Performances of the Vulcanized Silane Modified Epoxy Resins

Both the transparency and the yellowness index of the cured materials are significant impact factors for LED filament bulb package. The materials cured by various curing agents exhibited fairly high transparency as shown by Fig. 6. The yellowness index (Table 2) for the material cured by PEA-230 was the lowest, which indicated that the anti UV ability of the material was the best. The tensile shear test for the cured materials obtained by various curing agents is summarized in Table 3. As can be seen, the cured materials had good adhesive ability.

The effects of various R/Si and molecular weight of PEA on the vulcanized silane modified epoxy resins were investigated and the results are listed in Table 4. It can be seen that the hardness of the cured products decreased with

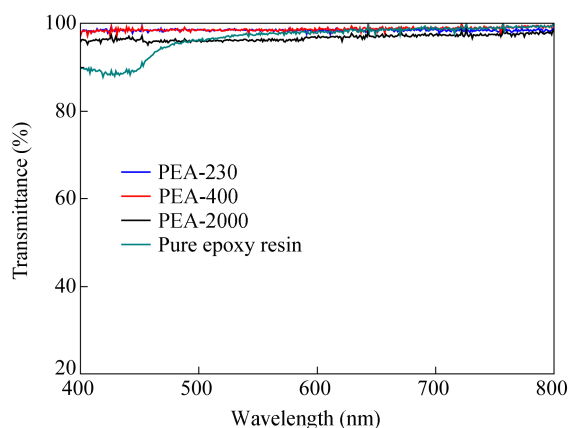


Fig. 6 The transparency of the cured materials obtained by various curing agents

Table 2 The yellowness index of the cured materials obtained by various curing agents

Sample	Transparency (%) at different wavelengths			YI (%)
	420 nm	560 nm	680 nm	
PEA-230	98.3	98.6	98.6	0.34
PEA-400	98.0	98.6	98.8	0.83
PEA-2000	96.3	96.4	97.2	0.91
Pure epoxy resin	88.6	97.8	98.6	10.20

Table 3 The tensile shear test for the cured materials obtained by various curing agents

Curing agent	Tensile strength (MPa)	Peel strength (N·mm ⁻¹)	Average tensile strength (MPa)	Average peel strength (N·mm ⁻¹)
PEA-230	0.41	5.3	0.46	5.8
	0.42	5.3		
	0.64	7.8		
PEA-400	0.37	4.8	0.80	10.5
	0.81	10.8		
	0.82	10.0		
PEA-2000	0.83	10.9	0.18	2.3
	0.76	9.6		
	0.16	2.2		
	0.22	2.5		
	0.16	2.1		
	0.19	2.4		

Table 4 Effects of various R/Si and molecular weight of PEA on the curing silane modified epoxy resins

Entry	Curing agent	R/Si	Hardness of the cured resins ^a (Shore A)
1	PEA-230	1.40	63
2		1.45	59
3		1.50	54
4		1.60	54
5		1.70	53
6	PEA-400	1.80	— ^b
7		1.60	54
8		1.60	44

^a Measured with an LX-X durometer. The silane modified epoxy resins were cured at 40 °C for 2 h, 60 °C for 1 h by PEA; ^b Could not be cured even over 24 h.

the increment of R/Si and molecular weight of PEA.

The DSC curves of the materials cured by PEA-230 with different r values are shown in Fig. 7. The exhibited fairly low glass transition temperatures denoted that the materials possessed good reflexivity^[22].

To analyze the structure of the cured products obtained, the FTIR spectra were measured (Fig. 8). As can be seen from the FTIR spectra in Fig. 8, the absorbance at 3430, 1097 and 906 cm⁻¹ attributed to the characteristic absorption peaks of OH, —Si—O—Si and epoxy respectively became faint after cured^[23].

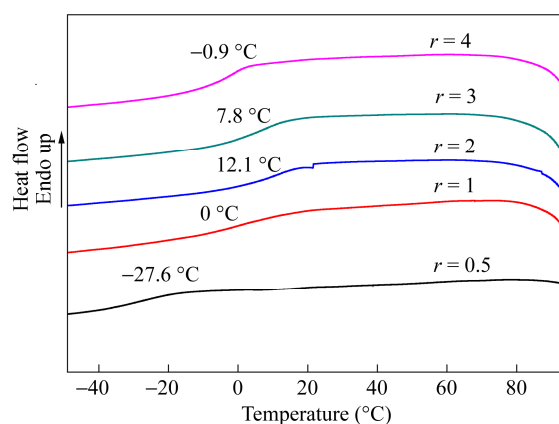


Fig. 7 DSC curves of the products with various r values

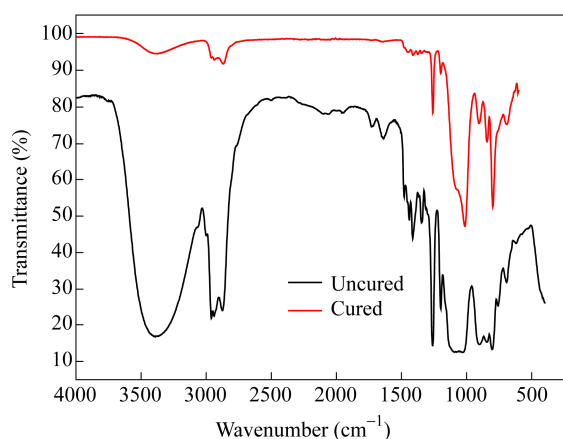


Fig. 8 FTIR spectra of the obtained silane modified epoxy resin before and after cured respectively

The Application of the Vulcanized Epoxy-modified Silicone Resin for LED Filament Bulb Package

Considering the results and discussions on the performance of the cured silane modified epoxy resins above, the silane modified epoxy resins cured by PEA-230 with $r = 1$ (Table S1, in ESI) was chosen to be the package material for an LED filament bulb test. The new resin was packaged on 11 pieces of the filament as shown in Fig. S3 (in ESI) and the photoelectric properties are given in Table 5. The experiments demonstrated that the effective luminous efficacy of the LED filament bulb packaged with the new resin was quite high (The average effective luminous efficacy was 110.65) and the silane modified epoxy resins prepared are good candidates for LED filament bulb package.

Table 5 The photoelectric properties of the filament packaged by the silane modified epoxy resin prepared

Entry	X	Y	CCT	Ra	Φ	VF
1	0.4605	0.4110	2695	81.6	111.3	77.8
2	0.4625	0.4132	2685	81.2	114.1	78.2
3	0.4611	0.4117	2692	81.4	111.8	78.0
4	0.4605	0.4105	2691	81.5	111.2	78.0
5	0.4597	0.4105	2704	81.7	112.0	78.3
6	0.4559	0.4077	2734	82.1	110.0	78.0
7	0.4553	0.4078	2743	82.2	109.2	77.8
8	0.4570	0.4098	2734	81.7	112.4	78.2
9	0.4577	0.4092	2720	81.9	108.5	77.8
10	0.4562	0.4073	2727	82.1	108.5	77.8
11	0.4551	0.4072	2741	82.2	108.1	77.8
AVG	0.4583	0.4096	2715	81.8	110.7	78.0

The LED chip was A17G-CD. VF = 3.05, WLD = 456.22, LOP = 23.97. The properties were measured at 10 mA. X and Y were x axis and y axis of Color coordinate respectively. CCT was colour temperature, Ra was rendering index, Φ was lighting effect and VF was forward voltage.

CONCLUSIONS

A new kind of low temperature vulcanized transparent silane modified epoxy resins for LED filament bulb package was prepared by an easily controlled sol-gel method. The

transparent silane modified epoxy resins cured by PEA-230 exhibited excellent thermal stability with thermal degradation temperature as high as 316.5 °C and adjustable hardness between 40–60 shore A. The application experiment showed the materials obtained were good candidates for LED filament bulb package. The ongoing research on the application of this kind of materials in 3D print and the other electric equipment package are also being carried out.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2028-8>.

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