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High refractive index and flame retardancy of epoxy thermoset cured by tris (2- mercaptoethyl) phosphate

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ABSTRACT

A novel curing agent containing phosphorus and sulfur, tris(2- mercaptoethyl) phosphate (TMEP), was designed and synthesized for LED packaging epoxy resin with high refractive index and good flame retardancy. The curing agent was prepared by sodium hydrosulfide method based on tris (2-chloroethyl) phosphate (TCEP) and sodium hydrosulfide. TMEP was mixed with triethylenetetramine and epoxy prepolymer at a certain ratio to generate cured samples. Fourier transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance (NMR) were employed to characterize the structure of the curing agent. The flame retardancy of the cured epoxy resin was determined by vertical burning test (UL-94) and limiting oxygen index (LOI) test. Its optical performance was examined by photoelectric haze meter and Abbe refractometer. The cured samples containing 21.6 wt% TMEP had UL-94 V0 rating and the LOI value of 29.2%. The results of scanning electron microscopy (SEM) and TGA demonstrated that TEMP could promote the formation of compact and continuous char foam layer during the combustion of the cured epoxy resin. The cured product containing 32 wt% TMEP yielded a light transmittance up to 92% and a refractive index as high as 1.593.

1. Introduction

In recent years, LEDs as a type of new solid light source have attracted increasing attention. However, difference between the refractive indexes of the encapsulating materials and LED dies can cause total internal reflection when light travels from the die into the encapsulant at certain incident angles, and hence results in low light output. To improve light extraction efficiency, the refractive index of encapsulating materials needs to be further improved [1].

The total electro-optical conversion efficiency of LED is approximately only 20%–30% due to its low efficiency of light extraction and other electric energy is converted into heat [2]. Heat impairs the performance of LED and increases the risk of a fire. In fact, LED-caused fires have become more frequently with the increase of LED applications. Therefore, LED encapsulation resin with good flame retardancy and high refractive index could improve the light extraction efficiency of LED and reduce the amount of heat released from the chip, extending the duration and reducing the possibility of fire.

Sulfur-containing groups, such as thioether, sulfone, thiophene, thiadiazole and thianthrene, were often utilized to increase the refractive index of optical resins [3]. A series of inorganic/organic hybrid polymers via thiol–ene click chemistry reaction can obtain high refractive index [4–6]. Because of the presence of highly polarizable main group elements such as Si, Ge, Sn, and S, the resulting polymers exhibited high refractive indexes ranging from 1.590 to 1.703.

Reactive phosphorus-containing flame retardants can efficiently improve the flame retardancy of polymer materials while having little impact on the physical and mechanical properties of materials. These flame retardants can form a sealed–structure carbonaceous foam layer on the combustion surface, acting as a flame retardant, oxygen barrier, smoke abater and drip preventer [7]. Xu

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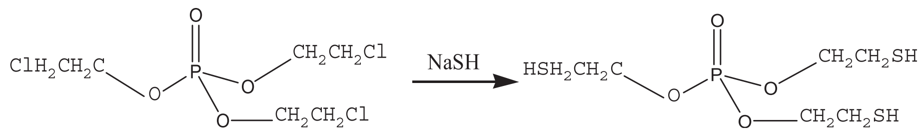

Scheme 1. Synthesis scheme of trimercaptoethyl phosphate (TMEP).

et al. successfully synthesized cyclotriphosphazene-based epoxy resin exa-[4-(glycidyloxycarbonyl) phenoxy] cyclotriphosphazene (CTP-EP) using hexachlorocyclotriphosphazene, phydroxybenzaldehyde and epichlorohydrin. All samples of CTP-EP cured with different curing agents can successfully pass UL-94 V0 rating [8]. A kind of new phosphorus-containing bio-based epoxy resin prepared by itaconic acid (IA) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) was synthesized and its cured epoxy showed good flame retardancy with UL94 V-0 grade [9]. D. Sun et al. synthesized three phosphorus-nitrogen flame retardant curing agents. When phosphorus content reached 1.0 wt %, epoxy resin system met UL-94 V-0 classification [10]. S. Yang et al. successfully synthesized a series of phosphorous/nitrogen-containing reactive flame retardants for epoxy resin system. The sample with phosphorus content of only 1.0 wt % achieved a UL94 V-0 rating [11,12]. A series of flame retardants containing sulfur, phosphorus, or nitrogen exhibited good flame retardant property [13]. Chen et al. synthesized bisneopentyl glycol dithiopyrophosphate (DDPS) and microencapsulated DDPS (MDDPS) with melamine formaldehyde (MF) resin [14]. MDDPS had good flame retardancy for PVA, and LOI of MDDPS/PVA composite was 31.8%. W. Zhao et al. synthesized a novel flame retardant containing phosphorus and sulfur, bis(2-tienyl)phenylphosphine (BTPP). Polycarbonate/3 wt% BTPP passed UL-94 V-0 rating with 3.0 mm samples and the LOI value was 36.5% [15]. K. Dai et al. synthesized a novel reactive phosphorus- and sulfur-containing flame-retardant monomer [di(allyloxybisphenol sulfone) phenoxy phosphonate, DASPP]. The resulting unsaturated polyester resin samples containing DASPP demonstrated significant enhancements in thermal properties, flame retardancy and mechanical properties [16]. Other studies had shown the efficiency of P–S–N flame retardants [17,18]. But these resins in the above works were not optical resins. Guo et al. prepared highly transparent and halogen-free flame retardants optical resins based on poly(methyl methacrylate) (PMMA) and two cyclotriphosphazene derivatives, but the refractive index were only from 1.497 to 1.532 [19].

Although optical resins with high refractive indexes or with halogen–free flame retardancy have been investigated, respectively, halogen–free flame retarded resins with high refractive indexes have rarely been reported. In the present study, sodium hydrosulfide was allowed to react with trichloroethyl phosphate (TCEP) in order to synthesize tris(2-mercaptoethyl) phosphate (TMEP), a S–P flame retardant curing agent for epoxy prepolymer. This kind of reactive flame retardant curing resin can efficiently improve not only the flame retardancy of cured epoxy resin, but also the refractive index of cured epoxy resin.

2. Experimental

2.1. Materials

Trichloroethyl phosphate (TCEP) was purchased from Zhengtong Chemical Co., Ltd. (Guangzhou, China), sodium hydrosulfide from Jiaxin Chemical Co., Ltd. (Henan, China), epoxy NPEL-128 from Jiadida Chemical Co., Ltd. (Shenzhen, China), triethylene tetramine (TETA) (AR) and other common reagents (AR) from Guangfu Technology Development Co., Ltd. (Tianjin, China). All chemicals were used without further purification.

2.2. Preparation of trimercaptoethyl phosphate

After adding 9 g (0.03 mol) of TCEP to a three-necked flask, 100 mL of 1.5 mol/L aqueous solution of sodium hydrosulfide was added dropwise under agitation. After reacting thermostatically at 70 °C for 3 h, the mixture was placed in a separatory funnel overnight to separate the lower yellow oil layer. This layer was then filtrated and rinsed with distilled water. The resulting product was finally prepared through dehydration under a vacuum. The detailed synthetic route of this process is shown in Scheme 1.

2.3. Preparation of the cured samples

TMEP was mixed with triethylene tetramine (TETA) and epoxy prepolymer at a certain ratio, and the proportion of samples was shown in Table 1. After stirred and defoamed by an ultrasound device, the mixture was then poured into a silicone rubber mold for curing at 70 °C for 3 h. The resulting samples were able to be tested for their flame retardancy, refractive index and light transmittance.

2.4. Characterization

The chemical structures of specimens were measured by a Nicolet 6700 Fourier transform infrared spectra (FTIR) spectrometer. Thermogravimetric analysis (TGA) was carried out using a U.S. TA Instruments TGA Q50 analyzer. The samples were heated from 50 °C to 550 °C at a rate of 10 °C/min under the protection of nitrogen flow (balance purification velocity is 40 mL/min, flow rate in the sample room is 60 mL/min). The every specimen in TGA was about 5 mg of bulk solid. UV–Vis Transmittance spectra was recorded with a UV1801 UV–Vis scanning spectrophotometer for the sample with a thickness of 1 mm. The refractive indexes of samples were determined using a WYA Abbe refractometer.

The limiting oxygen index (LOI) values were measured on a JF-3 oxygen index instrument (Jiangning, China) in order to evaluate flame retardancy of samples with sheet dimensions of $130 \times 6.5 \times 3$ mm^3 according to ISO 4589-2:1996. The vertical burning ratings were measured on a CZF-2-type instrument (Jiangning, China) with sheet dimensions of $130 \times 12.5 \times 3$ mm^3 according to American National Standard ANSI/UL 94-2010. Scanning electron microscopy (SEM) (Inspect F, FEI Co., Ltd.) was used to observe the morphology of samples based on an accelerated voltage of 5.0 kV.

Table 1
The mass ratio of the samples.

Samples	Formula (with a small amount of TETA accelerator)		
	Epoxy prepolymer (g)	TETA (g)	TMEP (g)
①	1	0.140	0
②	1	0.086	0.5
③	1	0.072	0.5
④	1	0.051	0.5
⑤	1	0.043	0.5