A study of ultraviolet-curable organic/inorganic hybrid nanocomposites and their encapsulating applications for organic light-emitting diodes

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ABSTRACT

UV-curable organic/inorganic hybrid nanocomposites have been successfully synthesized with polymer monomers (tetramethoxysilane (TMOS)/3-glycidoxypropyl-trimethoxysilane (GPTMS)) nano-fillers (silica/alumina), curing agents (bisphenol A (BPA)), and photoinitiators (triaryl sulfonium hexafluoroantimonate (TSH)) by in situ polymerization. Their thermal stability, coefficient of thermal expansion (CTE), adhesion strength, and gas barrier capability have also been investigated with thermogravimetry analysis (TGA), thermomechanical analysis (TMA), micro-computer universal testing machine and moisture penetration tests. Experimental results indicate that nano-fillers are completely homogeneously dispersed in the polymer matrices and the increase of nano-fillers in the nanocomposites causes the raise of decomposition temperature (T_d) as well as gas resistance and the reduction of CTE as well as adhesion strength. Because lab-made organic/inorganic hybrid nanocomposites have been discovered to exhibit excellent gas barrier properties, we have also applied them for the encapsulation of organic light-emitting diodes (OLEDs) and flexible OLEDs. With lab-made nanocomposite d, the lifetimes of OLEDs and flexible OLEDs can be successfully lengthened to 92 and 36 h, respectively, whereas those of OLEDs and flexible OLEDs without encapsulation are 11 and 7 h, respectively.

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1. Introduction

Organic/inorganic hybrid nanocomposites are composed of organic polymer matrices (e.g. acrylics, epoxy, and silicone, etc.) as well as inorganic nano-fillers (e.g. silica (SiO_2), titanium oxide (TiO_2), zinc oxide (ZnO), and alumina (Al_2O_3), etc.) [1] and have drawn considerable attention because of their excellent mechanical strength, thermal stability, electrical properties, and resistance of staining [2–4]. Furthermore, organic light-emitting diodes (OLEDs) have also attracted much attention in recent years due to their widespread applications for illumination as well as displays [5] and possess the advantage of higher contrast ratio, lower cost, better brightness, less power consumption, larger viewing angle and faster response time [6–8]. However, their lifetimes have recently become an essential issue for practicability since oxygen and moisture in the air induce the corrosion of organic layers and metal electrode, dropping the lifetimes dramatically [9,10]. Without high-performance encapsulating adhesives, the lifetimes of devices are limited.

Although organic/inorganic hybrid nanocomposites have been utilized in biological, mechanical, and electronic regions [11–13], the studies about their encapsulating application are less reported.

In this paper, ultraviolet (UV)-curable organic/inorganic hybrid nanocomposites have been synthesized with silicone-epoxy monomers, nano-fillers (silica/alumina), curing agents, and photoinitiators via in situ polymerization. Because experimental data represent lab-made nanocomposites possess good thermal stability, adhesive properties, and gas barrier capability, we have then fabricated OLEDs as well as flexible OLEDs and applied them for the encapsulation. Experimental results manifest lab-made organic/inorganic hybrid nanocomposites are excellent encapsulating adhesives and effectively prolong the lifetimes of OLEDs as well as flexible OLEDs.

2. Experimental

2.1. Materials

Tetramethoxysilane (TMOS) and 3-glycidoxypropyl-trimethoxysilane (GPTMS) were utilized as monomers for silicone-epoxy polymer matrices and purchased from Fluka Co. The chemicals used for OLEDs and flexible OLEDs (i.e. naphthyl phenyl benzidine (NPB; hole transport material), tris-[8-hydroxyquinoline] aluminum (Alq_3;

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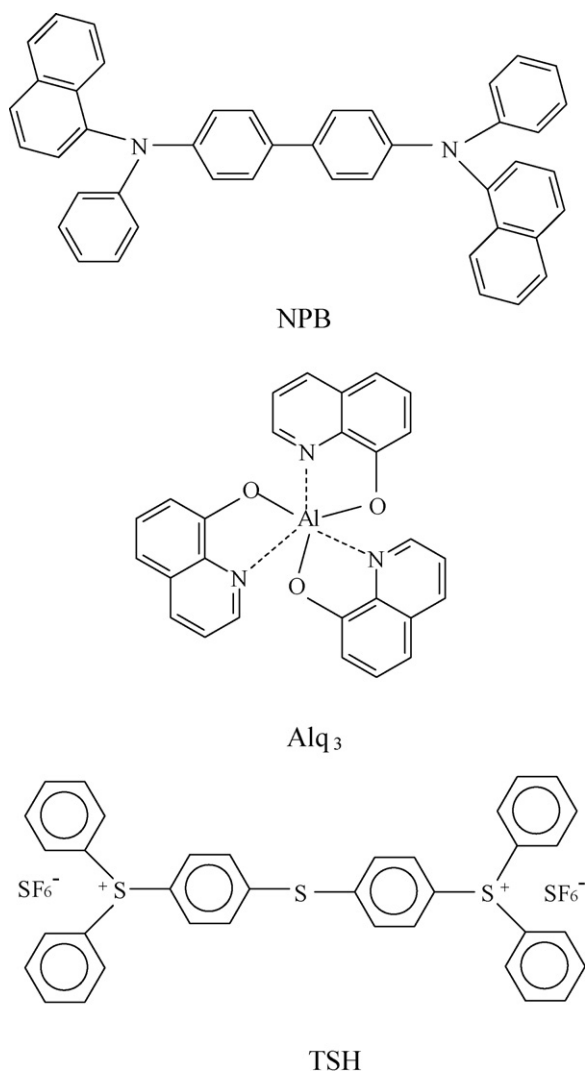
NPB

Alq₃

TSH

Fig. 1. Chemical structures of NPB, Alq₃, and TSH.

light-emitting material), and lithium fluoride (LiF; electron injection material), bisphenol A (BPA; curing agent), triaryl sulfonium hexafluoroantimonate (TSH; photoinitiator), hydrogen chloride, and nano-filler (silica/alumina) were obtained from Aldrich Co. (Fig. 1). All the materials in this study were utilized without further purification.

2.2. Preparation of UV-curable organic/inorganic hybrid nanocomposites (Scheme 1)

GPTMS and TMOS were firstly mixed (2:1 molar ratio) in a beaker with 0.01 M HCl and methanol (1:2 molar ratio) at ambient temperature. The resultant two-phase solution was mechanically stirred at a rate of 240 rpm for 1 h to complete hydrolysis and condensation of the silane. Then BPA (10 wt%), silica (30 wt%), alumina (5–15 wt%), and TSH (1 wt%) were added to the solution. After mechanically stirred at a rate of 240 rpm for 4 h, the transparent UV-curable organic/inorganic hybrid nanocomposites without phase separation were synthesized (nanocomposite a: polymer matrices/silica (30 wt%)/alumina (0 wt%); nanocomposite b: polymer matrices/silica (30 wt%)/alumina (5 wt%); nanocomposite c: polymer matrices/silica (30 wt%)/alumina (10 wt%); nanocomposite d: polymer matrices/silica (30 wt%)/alumina (15 wt%)). The viscosities of lab-made nanocomposite a, b, c, and d were 12,500, 12,800, 13,200, and 13,700 cps, respectively.

2.3. Instruments

Thermal characterization and viscosity were measured by a DuPont 2950 thermogravimetric analyzer (TGA) at a heating rate of $10\,°C\,min^{-1}$ in the air and a Viscolite 700, respectively. The coefficient of thermal expansion (CTE) was investigated by an in-plane thermomechanical analysis (TMA; DuPont 2940) with a micro-expansion probe at a heating rate of $10\,°C\,min^{-1}$. Moreover, we also examined the microstructures, gas penetration, and adhesion strength with a transmission electron microscope (TEM; Philips TECNAI G2) operating at 200 kV, Illinois-8501, and a micro-computer universal testing machine (Hung Ta Co.), respectively. The UV lamp used for UV-curing was an Entela UVP 100W. In addition, we recorded the electroluminescent effects and lifetimes of OLEDs by Keithley 2400 and Spectrascan PR650, respectively (Fig. 2). The electrical conducting properties were investigated with a 4-point probe (Everbeing SR-4). The thickness of encapsulating adhesive was measured by a surface profiler (TENCOR P-10).

2.4. Fabrication of OLEDs and flexible OLEDs

The indium tin oxide (ITO) glass ($5\,\Omega/\square$) was ultrasonically washed with the acetone, methanol, and de-ionized water for 5 min. After dried with a stream of nitrogen as well as the oven and treatment of O_2 plasma for 90 s, we deposited NPB (hole transport layer; 50 nm), Alq₃ (light-emitting layer; 50 nm), LiF (electron injection layer; 3 nm), and Al (cathode; 80 nm) layer by layer onto the ITO glass with vacuum evaporation. Finally, lab-made organic/inorganic hybrid nanocomposites (100 μm) were deposited on the Al electrode by spin-coating technique (stage I: 1500 r.p.m. for 20 s; stage II: 3500 r.p.m. for 30 s) and cured by UV illumination for 10 s (Fig. 3(a)). The similar process was executed in the fabrication of flexible OLEDs except the ITO glass was replaced with the ITO PET (poly(ethylene terephthalate)) (Fig. 3(b)).
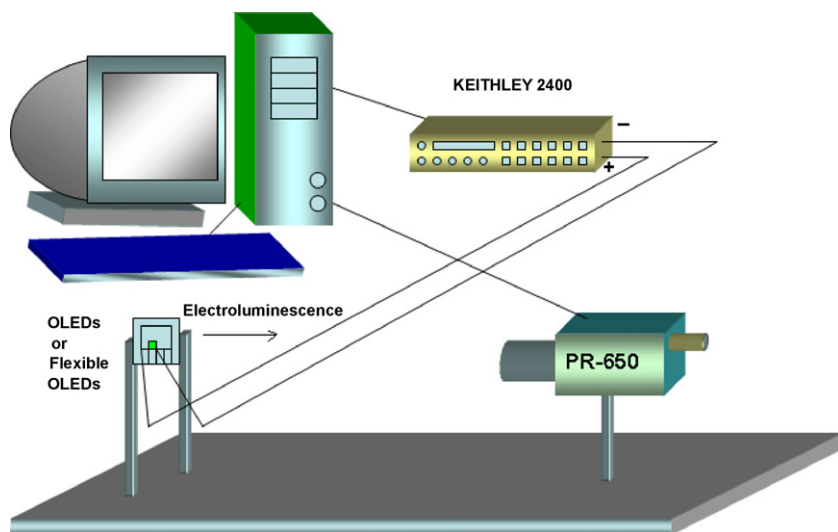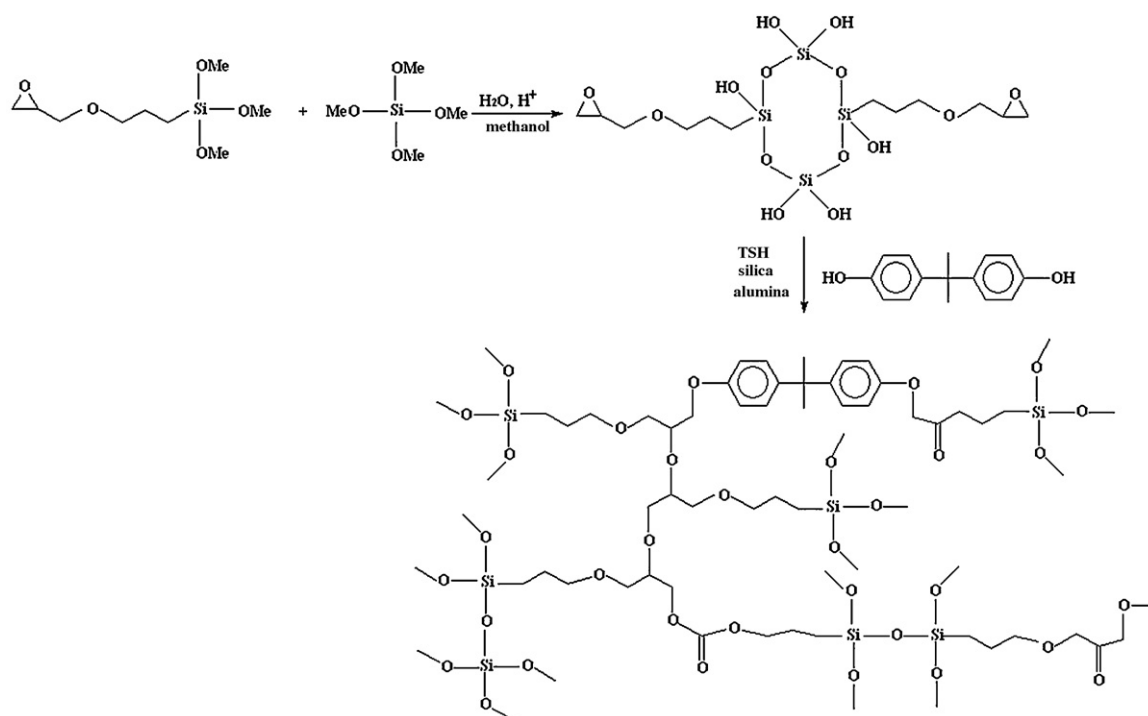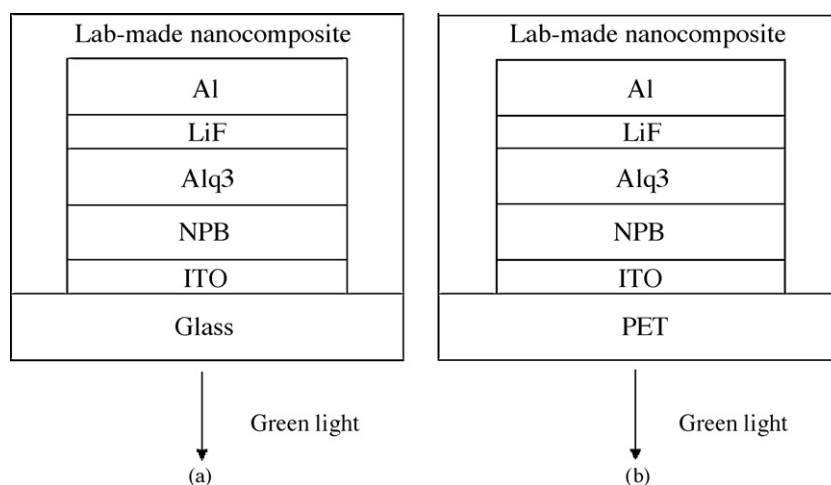

Fig. 2. The measurement system for electroluminescent effects and lifetimes of lab-made OLEDs.

Scheme 1.

Fig. 3. Structures of lab-made OLEDs and flexible OLEDs. (a) ITO glass/NPB (50 nm)/Alq$_3$ (50 nm)/LiF (3 nm)/Al (80 nm)/nanocomposite (100 μm); (b) ITO PET/NPB (50 nm)/Alq$_3$ (50 nm)/LiF (3 nm)/Al (80 nm)/nanocomposite (100 μm).

3. Results and discussion

3.1. UV curable organic/inorganic hybrid nanocomposites

Epoxy and silicone resins [14] are well-known polymeric materials for electronic, mechanic, and biological industrials due to their chemical modifiability, high transparency, and good processability.

Nonetheless, discoloration takes place while epoxy polymers are cured at high temperature and silicone polymers have high cost and weak reactivity, causing their long curing duration. In order to achieve a compromise, therefore, we have combined these two materials to silicone-epoxy polymers, which possess no color stain at high curing temperature, moderate cost, and short curing time. Via in situ polymerization, furthermore, silicone-epoxy polymer

Table 1
Thermal, gas barrier, and adhesive properties of lab-made organic/inorganic hybrid nanocomposites.

Sample	T_d[a] (°C)	CTE$_{40-100\,°C}$ (ppm °C^{-1})	Gas permeability (%)	Adhesion strength (kgf cm^{-2})
Nanocomposite a	305	95.28	7.404	89.1
Nanocomposite b	315	94.20	5.312	70.4
Nanocomposite c	320	80.96	3.304	65.7
Nanocomposite d	328	76.62	1.104	53.8

[a] The values of T_d were 5% weight loss at TGA curve with a heating rate of 10 °C min^{-1}.
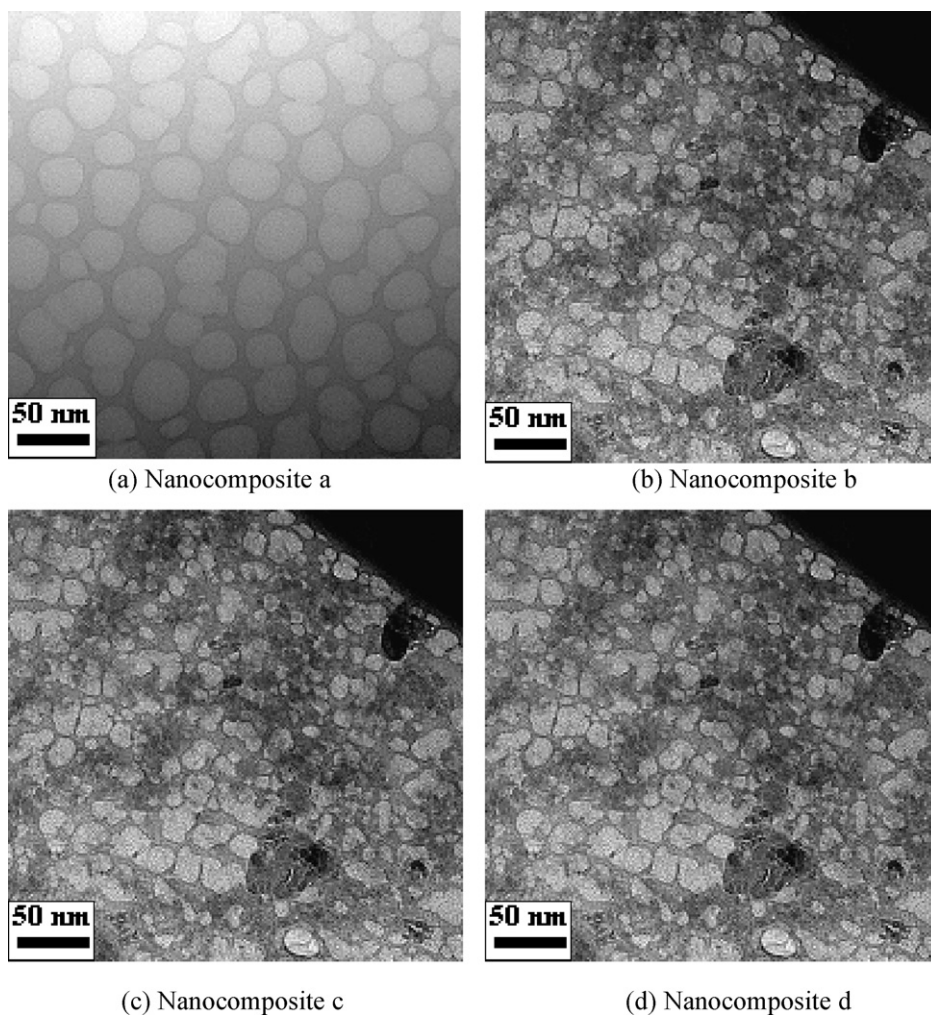
Fig. 4. TEM results of lab-made organic/inorganic hybrid nanocomposites. (a) Nanocomposite a, (b) nanocomposite b, (c) nanocomposite c, and (d) nanocomposite d.

monomers are blended with nano-fillers (silica/alumina), curing agents, and photoinitiators to form UV curable organic/inorganic hybrid nanocomposites as shown in Scheme 1 and nano-fillers were completely homogeneously dispersed in the polymer matrices as shown in the TEM results (Fig. 4).

The curing duration for lab-made organic/inorganic hybrid nanocomposites with the irradiation of UV is 10 s while that with conventional thermal method is several hours. With UV procedure, the whole production efficiency can be promoted and the product is immediately ready for testing, shipment, and storage rather than a multi-step thermal drying process. Moreover, UV procedure has lower energy consumption and is also an environment-friendly technology without emissions of volatile organic compounds (VOCs) and flammability.

3.2. Thermal properties and electrical insulation

Fig. 5 indicates the thermal characterization of lab-made organic/inorganic hybrid nanocomposites. As shown in Table 1, the decomposing temperature (T_d; 5 wt% weight loss) of nanocomposite a is approximately 305 °C. When 5, 10, and 15 wt% of alumina were added, nevertheless, their T_d raise and reach 315, 320, 328 °C, respectively. The improvement of the thermal properties was attributed to the high thermal stability of nano-fillers (silica/alumina). The CTE of lab-made organic/inorganic hybrid

nanocomposites are also shown in Fig. 6 and tabulated in Table 1. We observe that the CTE decrease with the increase of alumina because the epoxy network with high amounts of nano-fillers rises the crosslinking portions and forms rigid structure, leading to the decline of CTE.
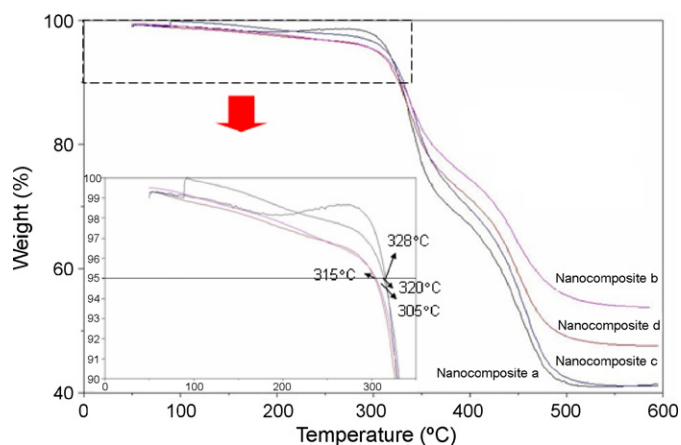
Fig. 5. TGA curves of lab-made organic/inorganic hybrid nanocomposites under air.
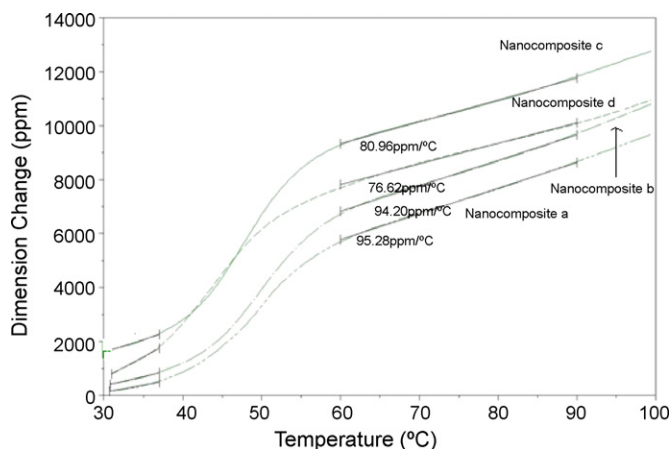
Fig. 6. TMA curves of lab-made organic/inorganic hybrid nanocomposites.

The electrical conductivities of lab-made organic/inorganic hybrid nanocomposites have also been investigateed. According to the experimental results of electrical resistance measurement, all of lab-made organic/inorganic hybrid nanocomposites have no electrical conductivities. The electrical insulation of nanocomposites may avoid electrical interference of devices while they are applied for encapsulating adhesives.

3.3. Gas permeability and adhesion strength

As shown in Table 1, the gas permeability and adhesion strength decrease with the increase of alumina since nano-fillers exhibit excellent resistance to gas penetration and low surface energy with the glass. In case of nanocomposite d, its gas permeability and adhesion strength can reach 1.104% and 53.8%, respectively.

3.4. Encapsulation of OLEDs and flexible OLEDs with organic/inorganic hybrid nanocomposites

Since nanocomposite d has best gas barrier capability among all of lab-made organic/inorganic hybrid nanocomposites, we have utilized it for the encapsulation of OLEDs and flexible OLEDs. In case of OLEDs without encapsulation, as shown in Fig. 7, the luminance sharply reduces while the device is actuated and the half-lifetime, defined as the duration when the luminance decays from the orig-
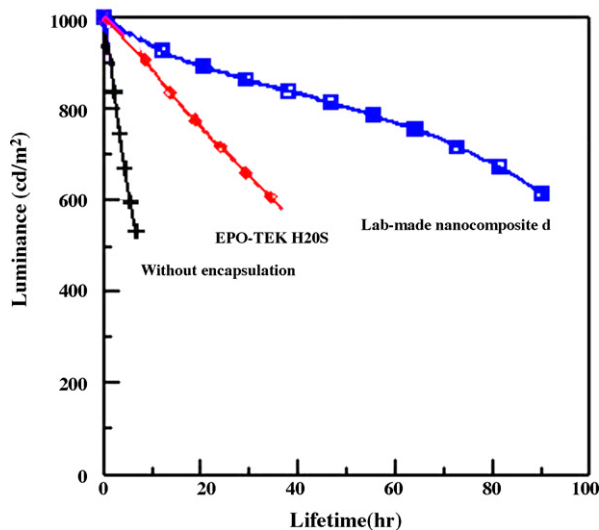

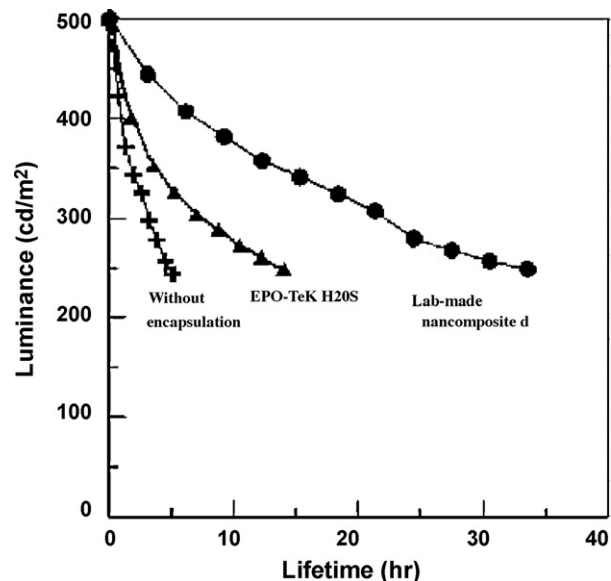**Fig. 7.** The lifetimes of lab-made OLEDs.

Fig. 8. The lifetimes of lab-made flexible OLEDs.

inal amount to its half, is only 11 h, representing the oxygen and moisture in the air cause the corrosion for metal electrode and organic layers. Nevertheless, the half-lifetime dramatically rises to 92 h while nanocomposite d is encapsulated in the device. This result manifests organic/inorganic hybrid nanocomposites can resist the penetration of moisture and oxygen in the air into the OLEDs, quenching the degradation of metal electrode as well as organic materials and rising the lifetimes. Compared with commercial UV curable encapsulating adhesive (EPO-TEK H20S; Epoxy technology Inc.), lab-made nanocomposite d has shorter curing time and longer lifetime because the half-lifetimes and curing time of OLEDs with EPO-TEK H20S are 43 h and 3 min, respectively.

The similar result can be found in the case of flexible OLEDs (Fig. 8). The half-lifetimes of flexible OLEDs with the encapsulation of nanocomposite d is 36 h, which is 5.1 and 2.7 folds longer than those without encapsulation and with EPO-TEK H20S, respectively. This result demonstrates organic/inorganic hybrid nanocomposites exhibit excellent gas blocking effect, promoting the lifetimes of flexible OLEDs.

4. Conclusions

We conclude that UV curable organic/inorganic hybrid nanocomposites with high thermal stability, fast curing time, good adhesion strength, moderate CTE, and excellent gas resistance have been successfully prepared by in situ polymerization. Furthermore, they have also been proved to be a superior material for encapsulation of electronic devices since the lifetimes of OLEDs and flexible OLEDs with encapsulation are 8.4 and 5.1 times longer than those without encapsulation, respectively.

Acknowledgement

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