

STUDY OF DEGRADATION MECHANISM AND PACKAGING OF ORGANIC LIGHT EMITTING DEVICES

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Abstract Organic Light Emitting Devices (OLED) have attracted much attention recently, for their applications in future Flat Panel Displays and lighting products. However, their fast degradation remained a major obstacle to their commercialization. Here we present a brief summary of our studies on both extrinsic and intrinsic causes for the fast degradation of OLEDs. In particular, we focus on the origin of the dark spots by “rebuilding” cathodes, which confirms that the growth of dark spots occurs primarily due to cathode delamination. In the meantime, we recapture the findings from the search for suitable OLED packaging materials, in particular polymer composites, which provide both heat dissipation and moisture resistance, in addition to electrical insulation.

Keywords Organic light emitting devices, Degradation mechanism, Dark spots, Cathode rebuilding, Polymer composites, Heat dissipation and moisture resistance

INTRODUCTION

Over the last several years, Organic Light Emitting Devices (OLED) have become a subject of intensive research in universities and industrial laboratories worldwide. This is a new type of electronic device that offers many advantages over the existing information display technologies: they can be made into very thin, sheet-like flat panel displays of large sizes, to replace the bulky vacuum picture tubes (CRT) in today's TV and computer monitors; they only require the voltage provided by a few flashlight batteries, instead of tens of thousands of volts needed by a CRT, which was also responsible for the unwanted radiation; they surpass both semiconductor light-emitting diodes, which are expensive, and the liquid crystal displays (LCD) which have a limited viewing angle and need to be illuminated.

This is a subject of both interesting science and immediate market, estimated at over US\$ 25 billion/year for the flat panel displays alone, and at least double that figure if CRTs are included, in addition to other applications of display devices, such as in phones, pagers and even toys.

Although efficient electro-luminescence from a multi-layer organic device was first reported in 1987^[1], the real sensation did not start until the beginning of 1990 when the Cavendish group fabricated poly(*p*-phenylene-vinylene) (PPV) thin films exhibiting electro-luminescence^[2]. The field has grown so rapidly ever since, that by 1999, there were over 1,000 published journal papers plus many conference proceedings^[3].

In the meantime, the performance of OLEDs has been improved drastically, from 1 lm/Watt for small molecules and 0.1 lm/Watt for polymers, to over 10 lm/Watt for both types. Because of their high brightness and energy efficiency^[4], and the availability of a wide range of emission colors^[5, 6], OLEDs have great potential to achieve low-cost, full-color flat-panel displays.

However, they show relatively poor stability. The half-lifetime, defined as the time elapsed before the

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luminance of the OLED decreases to half its initial value, usually amounts to only a few thousand hours^[6], as compared to a normal CRT which can last for over 100,000 h. In general, degradation in OLEDs occurs through the formation of non-emissive “dark” spots, as well as through a long-term “intrinsic” decrease in the electro-luminescence (EL) efficiency of the devices during operation^[7].

Although it was claimed recently, that over 50,000 h lifetime has been achieved, mostly such results reflect only the testing data obtained under accelerated conditions^[8, 9]. This is because one has only 8640 h per year, and it would take continuously 6 years to reach 50,000 h. Therefore, people usually run OLEDs at more than 10–20 times the desired luminance, and then scale up the operation time in proportion. In practice, however, this is not acceptable because dark spots and other extrinsic degradation will develop and kill the device even during their shelf life, or non-operative states. Therefore, it remains as a major challenge to increase the long term stability^[10].

DEGRADATION MECHANISMS

Our group first started its investigation back in 1992–1993, when we studied polymeric OLEDs^[11, 12]. Within a few years we discovered some major causes for the fast degradation of polymer based OLEDs^[13, 14]. We then joined the small molecule OLEDs research effort of Xerox Research Center of Canada. Some important discoveries were made, including both the extrinsic and intrinsic degradation mechanisms for small molecule based OLEDs^[15–18].

Apart from the degradation mechanism studies of polymeric based OLEDs^[13, 14], we have also studied tris-(8-hydroxyquinoline)aluminum (Alq₃) films and their electro-luminescence, photoluminescence by electron and optical microscopy and atomic force microscopy, and microscopic infrared spectroscopy. It was found that humidity induces the formation of crystalline Alq₃ structures in originally amorphous films. The same phenomenon is found to occur in OLEDs and causes cathode delamination at the Alq₃/cathode interface that results in the formation of black (non-emissive) spots in the devices^[15].

Shortly afterwards, another phenomenon was observed, that a majority of the non-emissive spots are caused by the growth of Mg(OH)₂ sites at the Alq₃/Mg:Ag interface, associated with local degradation of the Alq₃ layer. In addition, the growth of elevated cathode bubbles, which also leads to non-emissive spots, is found to be caused by gas evolution from the galvanic corrosion of the Mg/Ag couple as well as from the electrolysis of absorbed moisture^[16].

Moreover, it was found that injection of holes in Alq₃ is the main cause of “intrinsic” device degradation. The transport of holes into Alq₃ caused a decrease in its fluorescence quantum efficiency, thus showing that cationic Alq₃ species are unstable and that their degradation products are fluorescence quenchers. These findings explain the success of various approaches to stabilizing OLEDs, such as doping of the hole transport layer, introducing a buffer layer at the hole-injecting contact, and using mixed emitting layers of hole and electron transporting molecules^[17].

More recently, some critical phenomena were observed, which revealed the origin of the dark spots, the major cause of OLED failure^[18]. It has been known that the exposure to ambient conditions leads to the formation of non-emissive areas (dark spots) that result in a decrease in device luminescence. In this study, optical microscopy is used to investigate the sites of dark spots of devices in which the original cathodes are peeled off and replaced by newer cathodes. Results confirm that the growth of dark spots is associated with changes in the organic layers, especially at the organic/cathode interface (Figs. 1a–1d). Results also suggest that the nucleation of dark spots takes place at the organic/cathode interface and originates during the deposition of the cathode. On the other hand, both the anode and the hole transport layer do not appear to play a role in the formation of dark spots.

PACKAGING MATERIALS

Accompanying the rapid growth of the electrical/electronics industry, there is an increasing demand for better packaging materials, especially for those having specific physical properties in combination with electrical

insulation^[19]. For example, in order to extend the life-time of the recently developed organic light-emitting display (OLED) devices, the packaging material must fulfill a number of functions, such as, heat dissipation, moisture resistance and electrical insulation^[20]. The combination of these conflicting properties can be achieved by composites, often with polymers as the matrix due to the simplicity and rapidity with which they can be processed and applied. To enhance the intrinsically low thermal conductance of the polymers, ceramic powders are usually used as fillers in the composites. However, these composites may have very different moisture resistance from that of the parent polymers, due to the presence of polymer-filler interfaces^[21]. Moreover, their electrical insulation will be altered by the presence of the second or even third phases^[22].

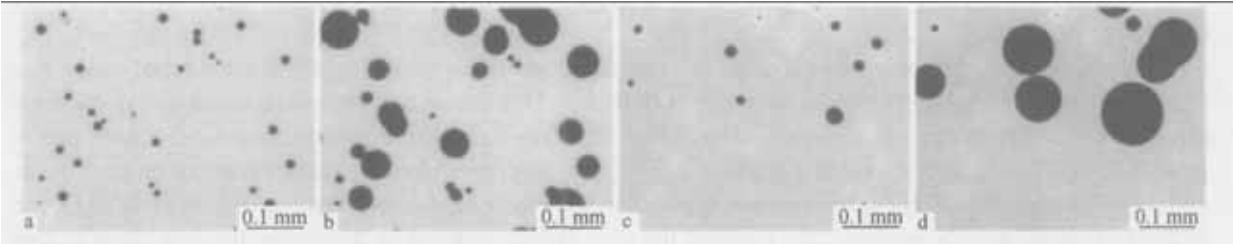


Fig. 1 Optical micrographs of OLED viewed under its own EL right after the device is made (a), after storing for 24 h in ambient conditions (b), the same OLED viewed after the second cathode is deposited (c), and after storing for 48 h in ambient conditions

To resolve these issues, studies were carried out for polymer composites on their thermal conductivity and moisture uptake. Three sample systems were measured: polyurethane (PUR) mixed with alumina powders (Al_2O_3), polyurethane with carbon fibers (CF), and silicone polymer (SIL) with boron nitride powders (BN). The results show that the combination of SIL/BN gives the highest thermal conductivity, the lowest moisture permeability and the least influence on dielectric loss tangent^[23, 24].

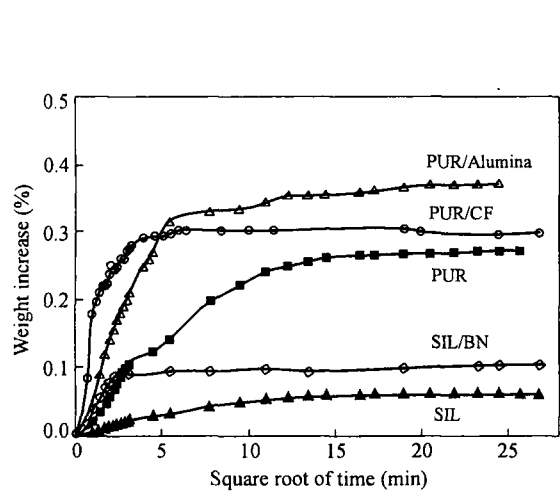


Fig. 2 Percentage of weight gain of (a) PUR/ Al_2O_3 , 18 vol%, (b) PUR/CF, 18 vol%, (c) SIL/BN, 18 vol%, (d) polyurethane, and (e) silicone as a function of time when exposed to water vapor (25°C, RH 40%)

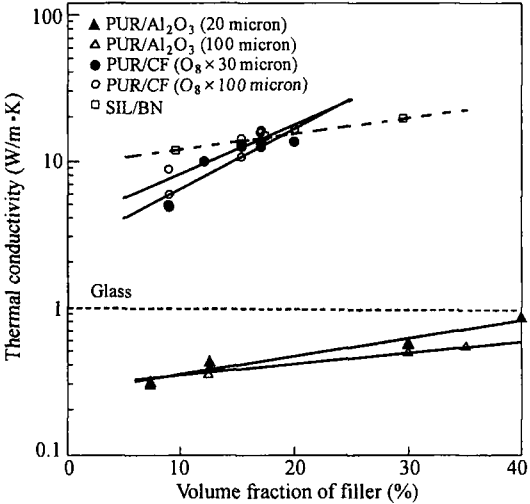


Fig. 3 Thermal conductivities of various composites

According to Fick's law, the sorption of moisture leads to a weight gain that is initially proportional to $t^{1/2}$. The rate of sorption falls off as saturation is approached and eventually produces a plateau. The weight percentage of moisture uptake of various polymers and composites were found to be in the range of

0.05%–0.35% by weight, as shown in Fig. 2. In particular, the moisture level in polyurethane reaches about 5 times that of pure silicone. However, the higher moisture sorption for the composites indicate that water molecules are absorbed not only by the polymer matrix, but also by the interfaces introduced by the fillers.

When fillers are mixed into the polymers, faster sorption takes place. Due to the crystalline nature of the fillers (therefore with negligible water uptake), the differences must come from the interfaces which are introduced by the mixing of filler particles or fibers. For example, alumina can not only chemically absorb moisture, but also has the ability to physically adsorb moisture to form $\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$. Although carbon fibers do not possess such capacity in the PUR/CF composite, the fibers perpendicular to the film surface will probably create some channels which allow for easier penetration of moisture, thereby producing faster water sorption kinetics than that of PUR/ Al_2O_3 .

In the meantime, the presence of ceramic powders or carbon fibers greatly improves the thermal conduction of pure polymers by mixing them into the polymer host (Fig. 3). Because of their special structure carbon fibers show greater ability to increase thermal conductivities of polymer composites which can reach 50 times that of pure PUR (11 W/mK at 25% volume fraction, see Fig. 3). And their electric conductivity can be kept below $10^{-8} \text{ S cm}^{-1}$, which is good enough for certain applications. The heat conduction behavior of both PUR/ Al_2O_3 and PUR/CF follows Agari's model^[25, 26]. Through the data fitting, parameters describing the formation of heat conduction "bridges" in the polymer composites, as well as the crystallisation of polymer chains, have been obtained which also have large effects on the thermal conductivity of polymer composites.

The dielectric relaxation spectroscopy shows the presence of a peak in the temperature range of 175–200 K, which is largely due to the moisture uptake. Compared with the PUR/ Al_2O_3 system, the dielectric loss property of PUR/CF under various humid environments at low temperatures (70–250 K) shows little change, and is thus not strongly affected by moisture uptake of polymer composites. However, the physical adsorption of moisture in the polymer composites might be the cause of an increase in the dielectric loss of PUR/ Al_2O_3 by up to 50%, in comparison to the dry sample^[24].

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