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Organic light-emitting diodes on shape memory polymer substrates for wearable electronics

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ABSTRACT

Green electrophosphorescent organic light-emitting diodes (OLEDs) with inverted top-emitting structures are demonstrated on bio-compatible shape memory polymer (SMP) substrates for wearable electronic applications. The combination of the unique properties of SMP substrates with the light-emitting properties of OLEDs pave to the way for new applications, including conformable smart skin devices, minimally invasive biomedical devices, and flexible lighting/display technologies. In this work, SMPs were designed to exhibit a considerable drop in modulus when a thermal stimulus is applied, allowing the devices to bend and conform to new shapes when its glass transition temperature is reached. These SMP substrates were synthesized using 1,3,5-triallyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (TATATO), trimethylolpropane tris(3-mercaptopropionate) (TMTMP), and tricyclo[5.2.1.0^{2,6}] decanedimethanol diacrylate (TCMDA), and show a low glass transition temperature of 43 °C, as measured using dynamic mechanical analysis (DMA). The OLEDs fabricated on these substrates exhibit high performance with a maximum efficacy of 33 cd/A measured at a luminance of 1000 cd/m^2, and a peak luminance of over 30,000 cd/m^2.

1. Introduction

Organic light-emitting diodes (OLEDs) have been attracting considerable interest lately due to their use in general lighting applications and full-color displays. Phosphorescent [1–5] and thermally-activated delayed fluorescent emitters [6,7] have been shown to produce internal quantum efficiencies (IQEs) close to 100%, which have led to highly efficient devices with current efficacies comparable to alternatives based on conventional inorganic LED technologies, and external quantum efficiencies (EQE) greater than 30% [5,8]. Moreover, OLED-based solid-state lights and color panels provide bright, efficient, extremely light-weight alternatives that can have flexible form factors [9]. Recently, our group was able to demonstrate highly efficient inverted top-emitting OLEDs based on an aluminum/lithium fluoride (Al/LiF) bottom cathode that produced current efficacies of over 200 cd/A at 1000 cd/m^2 [10–14]. This device architecture eliminates the need for an ITO bottom electrode and instead uses a vacuum deposited Al/LiF bottom cathode and semi-transparent gold (Au) top anode which allows for easy fabrication on flexible substrates. Unlike conventional bottom-emitting devices, the light exits the device through the top, semi-transparent Au anode which eliminates all substrates loses due to total internal reflection. Additionally, this device geometry is compatible with the industry preferred *n*-type driving transistors used in active matrix OLED (AMOLED) displays [11]. These devices have been successfully fabricated on flexible polymer substrates [such as polyethersulfone (PES)] and on recyclable nanocellulose/glycerol substrates in the past, which allowed for a limited deformation [11,15]. However, in order to fabricate solid-state lights and displays on truly conformable rather than deformable substrates, it is necessary to turn to a different group of substrates. In this paper, we extend this work and show the most efficient OLED produced on a shape-memory polymer (SMP) substrate for flexible and conformable wearable electronic applications.

SMPs are mechanically active, smart materials that have the unique ability to change modulus once an external stimulus is applied (such as temperature, electric potential, light, etc.) [16–18]. These stimuli allow the SMP substrate to exhibit a considerable drop in its modulus, after which the SMP rapidly softens to

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a rubbery state with a modulus up to three orders of magnitude lower than its original, glassy state. In this new rubbery state, the SMP can be easily deformed by external stresses into a temporary geometric configuration that can be retained even after the stress is removed by cooling the SMP to below T_g. Reheating the SMP causes strain relaxation within the polymer network and induces recovery of its original shape. These substrates have made a sizeable impact in solving neural interface issues for neural recording and stimulation applications [16–18] since the 'softened' state of the SMP has an elastic modulus that approaches that of human tissue. These unique mechanical properties can also be extended to a new branch of electronic device applications. The combination of these unique SMP properties with the light-emitting properties of OLEDs paves the way to a new branch of applications, including: comfortable smart skin devices, minimally invasive biomedical devices and flexible, conformable, and wearable lighting/display devices.

Yu et al. first reported the development of polymer light-emitting diodes on SMP substrates by using a single-walled carbon nanotube/polymer composite electrode as an indium tin oxide (ITO) replacement [19,20]. These devices produced a maximum current efficacy of 1.24 cd/A at 200 cd/m^2 with a turn-on voltage of 4.8 V, and a maximum luminance of 300 cd/m^2. In this paper, we show inverted top-emitting OLEDs fabricated in biocompatible SMP substrates that produced current efficacies of 33 cd/A at a high luminance of 1000 cd/m^2 with a low turn-on voltage of 3.4 V. Moreover, these devices can produce a maximum luminance of over 30,000 cd/m^2, making them ideal candidates for bioengineering applications that require high irradiance levels. These devices were fabricated via thermal evaporation directly on SMP substrates designed to exhibit a modulus drop at a T_g of 43 °C.

2. Experimental

2.1. SMP substrate synthesis

All polymer synthesis steps were performed in a fume hood. The substrates were fabricated using 1,3,5-triallyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (TATATO), trimethylolpropane tris(3-mercaptopropionate) (TMTMP), and tricyclo [5.2.1.0^{2,6}] decanedimethanol diacrylate (TCMDA) purchased and used as received from Sigma–Aldrich. The chemical structures for these monomers are shown in Fig. 1a. The monomers were mixed in a glass vial in a stoichiometric ratio of alkene to thiol groups (TATATO and TMTMP), with a further addition of 30 wt.% TCMDA. Prior to curing, an additional 0.1 wt.% 2,2-dimethoxy-2-phenylacetophenone (DMPA), as photoinitiator, was dissolved in the solution using a fixed-speed vortex mixer. The solution was then placed in an ultrasonic cleaner for 5 min to remove any trapped gasses.

Two clean glass microscope slides were cut to form a 1 × 1 in. mold area. The slides were cleaned by ultrasonication in acetone and isopropanol and blown dry with filtered nitrogen. The slides were then treated with two coats of a hydrophobic spray (Rain-X® Original Glass Treatment) to allow for the delamination of cured substrates. The slides were separated by glass spacers and clamped together to form a square mold with a thickness of approximately 1 mm. The monomer solution was injected to fill the mold using a glass Pasteur pipette. The solution was allowed to settle for 45 min and was cured under 365 nm UV light for 60 min. After curing, each polymer substrate was separated from its containing mold using a razor blade.

The cured substrates were exposed to oxygen plasma for 5 s. A film of poly(3,4-ethylenedioxythiophene)–polystyrene sulfonate (PEDOT:PSS Al 4083) was then deposited onto the substrates through a 0.45 μm polyvinylidene difluoride (PVDF) filter and spin coated at 5000 RPM for 60 s. Annealing was performed on a hot plate at 140 °C for 10 min.

2.2. OLED fabrication

OLED substrates consisting of 1.0 mm-thick glass micro-slides (VWR international) and 500 μm-thick SMP substrates were cut into 1 × 1 in. squares. The glass slides were then cleaned by ultrasonication (5510, Branson Ultrasonics) for 25 min in each of the following: water with detergent, distilled water, acetone, and isopropanol. The SMP substrates were briefly rinsed with isopropanol. The substrates were then blown dry with nitrogen before exposed to oxygen plasma (Plasma-Preen II, Plasmatic Systems, Inc) for 5 min. PEDOT:PSS Al 4083 was dispensed onto the substrates through a 0.45 μm PVDF filter and spin-coated (WS-400B-6NPP/LITE, Laurell Technologies, Inc.) at a speed of 5000 rpm for 1 min. The PEDOT:PSS-coated substrates were heated on a hot plate at 140 °C for 10 min. The PEDOT:PSS layer was measured to have a thickness of 40 nm by spectroscopic ellipsometry (M-2000UI, J.A. Woollam Co., Inc.). When deposited on glass, PEDOT:PSS has been shown to improve the device yield and reliability of electron-dominated diodes. The PEDOT:PSS improves the wetting of the bottom aluminum electrode.

The samples were then transferred to a high-vacuum thermal evaporation system (EvoVac, Armstrong Engineering Inc.). Once

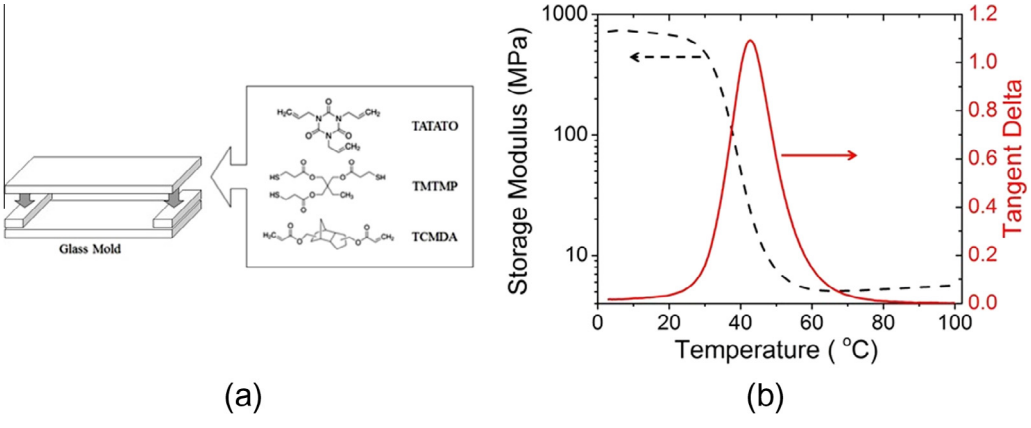

Fig. 1. (a) (Left) Graphical illustration of the mold used to fabricate SMP substrates. (Right) Chemical structure of monomers used in SMP synthesis. (b) Shear dynamic mechanical response of the synthesized SMP substrate. Black dotted line represents storage modules (MPa) versus temperature (°C). Red solid line represents tangent delta versus temperature (°C). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)