



## Towards colorless polyimide/silica hybrids for flexible substrates



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### ABSTRACT

In this work, we report highly transparent flexible polyimide/silica hybrids with low coefficient of thermal expansion (CTE) comparable to that of a glass, low optical birefringence and high thermal stability over 400 °C. We started from the polyimide system based on 2,2'-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA)/2,2'-bis-(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB), which has high optical transparency for aromatic polyimides, utilized well-known simple strategy of using silane end-capped oligomeric polyamic acid and silica sol-gel reaction to increase the miscibility between PI and silica, and finely tuned the property by control of molecular weight and processing condition. The resulting hybrid film showed homogeneous surface after oxide deposition and annealing, and passed the repeated folding/unfolding test with more than 200,000 cycles. These finely tuned hybrid films are promising candidate for flexible transparent substrate especially for high temperature (>400 °C) electronic and optoelectronic manufacturing processes.

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### 1. Introduction

Organic electroluminescent displays (OLEDs) have attracted considerable interest owing to their promising applications in flat panel displays based on high brightness, a wide viewing angle, high power efficiency, a light weight, and a quick response time [1–4]. Along with the growth of OLED display industry, the interest in transparent flexible plastic substrates has also increased for next generation applications in the fields of displays and the aerospace industry, as plastic substrates may be used to build light-weight, conveniently portable devices, roll-up displays, or foldable displays, which can be readily attached to windows, instrument panels, or other curved surfaces [5–7]. With the recent development of semiconductor techniques, it is feasible to fabricate semiconductor devices on organic flexible substrates. So far, the use of flexible substrates for OLEDs has been restricted mainly to polyester films due to their excellent transparent property [8]. Although a lot of candidates for flexible substrates such as polyethylene terephthalate (PET) [9–11], polycarbonate (PC) [12,13], polypropylene adipate (PPA) [14], etc, were considered, these plastic substrates can be severely damaged at high temperature

(200–300 °C) that are used during the deposition process, mainly due to their intrinsic low thermal and mechanical properties compared to other inorganic or metal substrate [15,16]. In case of low-temperature poly-Si (LTPS) technology, the flexible substrate should withstand higher process temperatures (>400 °C) for high performance TFT backplane [17,18], which requires glass transition temperature ( $T_g$ ) of substrate polymer above 400 °C and maintaining low coefficient of thermal expansion (CTE) up to 400 °C along with high transparency.

In this regard, Polyimides (PIs) are the best choice for flexible substrate owing to their excellent thermal, mechanical, and electrical properties. For example, they can be used as insulation layers for semiconductor devices, or substrates for flexible printed circuits [19–22]. Recently, light and thin plastic substrates for displays are being actively developed, as portable device market expands. The substrate, where TFT is deposited, is one of the important components in display devices with determining the performance, reliability, and even the price of the devices [23].

However, most of aromatic PIs usually show considerable coloration ranging from pale yellow to dark brown especially at high temperatures (>300 °C), which hinders their use in flexible substrate for display device. In general, aromatic PIs are thought to absorb UV/Visible light through formation of a charge-transfer complex (CTC) between the diamine and the dianhydride where the former acts as an electron donor and the latter as an electron acceptor [24,25]. The synthesis of colorless transparent PIs has been achieved by the introduction of non-aromatic [26–28], fluorine

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[29,30], or sulfone [31] groups into the polymer main chain. Although the introduction of bulky side groups or kinked structured monomer units is analogous to reducing the concentration of CTC formations, the increased CTE caused by lowered packing density of films makes it difficult to obtain good overlay alignment in the TFT array during OLED fabrication process. Considering the high process temperature of TFT fabrication (>350 °C) and the existence of trade-off between CTC formation and low CTE, it doesn't seem that organic polymer itself could achieve physical property requirements such as high temperature transparency after process, low CTE up to 400 °C comparable to glass, high thermal stability, flexibility and low birefringence [32–34].

Polymer/inorganic hybrids are an alternative way to overcome trade-off and to attain colorless flexible substrate, because inorganic component compensate for insufficient thermal stability of organic material and at the same time, decreases the CTE of overall hybrid film. Previously, Polyimides-organosilicate hybrids with improved thermal and optical properties were reported [35–37], nevertheless the CTE of hybrid film was already high in the range between 50 °C and 150 °C. Other optical and physical properties were obtained after thermal treatment of PI substrate at 250 °C, which is far below process temperature (>350 °C). Polyimide-aramid-silica nanocomposites first aimed at high temperature processability (~400 °C) with inferior optical property compared to this work, preparation of which is similar to our sol-gel approach [38]. Even it is true that the more silica incorporation results in the better properties, it is difficult to incorporate enough silica particles into the polymer matrix due to phase separation. The choice of appropriate dianhydrides and diamines is one key to increase miscibility along with *in-situ* condensation of organosilicates. The curing condition is another key to control surface cracks during the condensation of organosilicates.

Here, we report the preparation of polyimide-silica hybrid nanocomposite with maximum silica content up to 37.8 wt% and with excellent thermal stability, low CTE, low birefringence and high transparency comparable to inorganic substrates, even after high temperature thermal curing (>400 °C). The effect of composition and molecular weight of polyimides, and hybrid film preparation condition on physical and optical properties of colorless polyimide/silica hybrids for flexible substrates was also studied.

## 2. Experimental

### 2.1. Materials

2,2'-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA, Daikin Industries), pyromellitic dianhydride (PMDA, TCI chemicals), 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA, Mitsubishi Chemicals), 2,2'-bis-(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB, Finechemicals), 3-aminopropyl triethoxysilane (APS, Aldrich, 99%), tetramethyl orthosilicate (TMOS, Aldrich, >99%), *N*-methyl-2-pyrrolidinone (NMP, Aldrich, HPLC, 99.9%) were used as received.

### 2.2. Synthesis of silane (APS) end-capped polyamic acid (PAA)

PI1-2 was synthesized as below. TFDB (12.1173 g, 0.0378 mol) was added to 87.55 g of NMP in a 250 ml three-neck double-walled reactor equipped with a mechanical stirrer and a nitrogen inlet. The mixture was stirred until the monomer was completely dissolved at room temperature and then 6FDA (17.8827 g, 0.0403 mol) was slowly added to the solution. The ratio between diamine/dianhydride is 0.94 and solid content is 25 wt%. The resulting mixture was stirred for 24 h under a nitrogen atmosphere to obtain anhydride-terminated oligomeric amic acid.  $\tau$ APS (1.0693 g, 0.0048 mol) was

added to the above solution and stirred for 4 h, until all the anhydride end groups turn into silane terminated groups. The silane end-capped polyamic acids with different ratios of dianhydride to diamine (0.93–0.97) were also synthesized for comparison with the same protocol (Table S1). Synthesis of silane end-capped polyamic acid (PI2, 6FDA/s-BPDA/TFDB = 20/80/95) followed the same procedure like PI1 synthesis. The amount of TFDB, NMP, 6FDA, s-BPDA and APS used for the synthesis was 12.7798 g (0.0399 mol), 93.6 g, 3.7324 g (0.0084 mol), 9.8878 g (0.0336 mol) and 0.9299 g (0.0042 mol), respectively, and sequentially added into the reactor.

### 2.3. Preparation of PI-silica hybrids

8.91 g of silane end-capped polyamic acid soln. (for example PI1-2) was placed into 20 ml vial. 8 ml of TMOS soln. (TMOS/NMP/DI water = 6.8/4/9.2 (v/v/v)) was added into the solution and stirred for 48 h to obtain silica sol-PAA hybrid. Different amount silica loading was attained by using different ratio of TMOS soln. The ratio of TMOS/NMP/DI water was always fixed at 6.8/4/9.2 (v/v/v). The compositions used for the preparation of hybrids are summarized in Table 1.

The mixture was dropped onto glass plates (5 × 5 cm) and spin-coated at a different rotational speed depending on the solution viscosity. The film thickness was targeted at  $10 \pm 1$   $\mu$ m. Spin-coated films were pre-dried on a heating plate at 100 °C for 15 min to evaporate remaining solvent. Then the film was annealed in furnace at 300 °C for 1 h with various heating rates (3–20 °C/min) to investigate the heating rate effect and then temperature was increased to 400 °C and kept for another 30 min. After cooling, the films were peeled off and characterized. The route for the preparation of PI/silica hybrids is presented in Scheme 1.

### 2.4. Oxide deposition

Silicon oxide films with 200 nm thickness, from a mixture of SiH<sub>4</sub>, NH<sub>3</sub>, N<sub>2</sub> and He gases, were deposited on PI coated glass (5 cm × 5 cm) using PECVD system (BMR's HiDepTm) at 350 °C. After oxide deposition, thermal annealing at 400 °C or 430 °C for 1 h was followed to duplicate the heat transfer to the contact surface from CVD chamber during high temperature TFT process.

### 2.5. Characterization

#### 2.5.1. Optical properties

Optical properties were measured by Konica Minolta CM36000D spectrophotometer in the transmittance opacity/haze mode (360–740 nm). The transmittance (%), haze and yellow index (YI) were calculated with the D65, ASTM-D1003 and D1925 standard methods, respectively.

The refractive indices and birefringence of hybrid films were measured by prism coupler (Metricon Model 2010/M) at a wavelength of 633 nm. The silica content was calculated by the Lorentz-Lorentz Equation (1):

$$\frac{n^2 - 1}{n^2 + 2} = \frac{n_s^2 - 1}{m_s^2 + 2} \times v_s + \frac{n_p^2 - 1}{n_p^2 + 2} \times v_p \quad (1)$$

where,  $n$ ,  $n_s$  and  $n_p$  are refractive indexes of hybrid film, silica and polymer, respectively.  $v_s$  and  $v_p$  are correspondingly the volume fractions of silica and polymer, respectively.

Optical microscope image were taken by Olympus System Microscopes BX51M.

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