P-28: The Effect of Thermal Shrinkage on Indium Tin Oxide Coated Polyethylene Terephthalate for Flexible Display Applications

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Abstract
The shrinkage of Indium Tin Oxide (ITO) coated Polyethylene Terephthalate (PET) for flexible display applications is investigated using a Thermal Mechanical Analyzer (TMA). The effect of temperature on the resistance of the ITO coated PET was measured using a custom built 4-wire resistance probe in a temperature enclosure. Thermal shrinkage of the substrate effects the resistance of the ITO and is temperature and substrate dependent. The shrinkage is also anisotropic with the greatest shrinkage in the machine direction. Shrinkage of up to 4% was obtained for samples maintained at 180° C. This shrinkage can greatly influence the reliability of the ITO layer and must be considered during fabrication of flexible displays.

1. Introduction
Recently there has been great interest in the display industry in pursuing the development of high performance, lightweight flexible displays for portable devices [1-9] such as Personal Digital Assistants (PDAs), digital cameras, camcorders, mobile telephones and remote control units. A number of these portable displays also incorporate a touch sensor which may include a PET coated ITO substrate.

Plastic displays have many attractive features compared to displays that use glass substrates such as robustness, weight saving, thinness and flexibility. If suitable roll-to-roll fabrication processes can be developed plastic displays, may become a low-cost high-performance display technology alternative and open up new product categories as flexible or rollable displays.

For plastic displays to become a commercial success it is important to use reliable flexible substrates. Plastics based conducting electrodes and thin film transistors (TFTs) are being developed. Wagner and co-workers have developed amorphous hydrogenated silicon (a-Si:H) TFTs on polyimide films (Kapton E DuPont) [10-11]. Polyimide is a high performance engineering polymer with a Young's modulus of 5 GPa. The excellent mechanical properties of the polyimide films lend themselves to fabrication of robust devices. For conducting electrode materials there is an additional constraint as compared to TFTs in that the substrate must also have excellent optical properties.

PET and polycarbonate are the two most widely used substrates for plastic display applications and have inferior mechanical properties to polyimide, but superior optical properties. ITO is commonly used as the conducting electrode material in flat panel displays and touchscreens because of its combination of high optical transmission and low resistivity [12]. While ITO has been deposited on glass for a number of years, more recently it has been used on polymer substrates in the touchscreen input device for PDAs [13] and is an important material in the quest for lighter more flexible, portable displays. The successful deposition of ITO has been reported using RF sputtering for a wide range of polymers: Polyethylene Teraphthalate (PET), Polycarbonate, Polytetrafluoroethylene (Teflon) and thermoplastic Polymethyl methacrylate (Perspex, plexiglas) [13-16]. ITO coated Polyethyleneterephthalate (PET) is now available commercially and is used in the touchscreens of handheld PDAs. The PET is most often coated in a roll-to-roll process using a DC magnetron sputtering system [13]. Typical values of sheet resistance required by the display industry range between 80 Ω/ and 500 Ω/ which corresponds to a range of thickness in the ITO layer of 5-150 nm. Any deterioration of this layer in-service is detrimental to the operation of the display device.

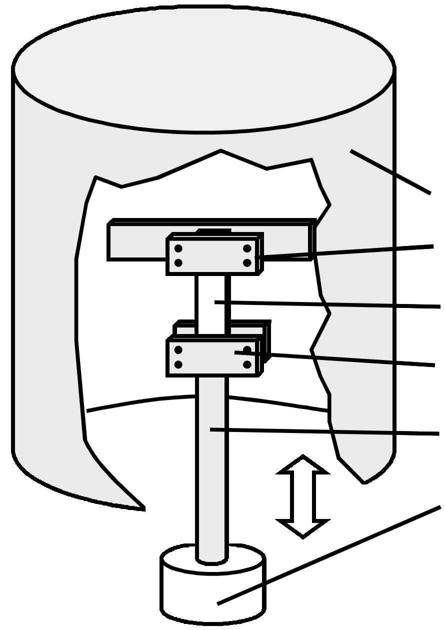

Figure 1 Schematic diagram of a Thermal Mechanical Analyzer showing the important components. Temperature and load can be controlled and displacement measured. Conversely temperature and displacement can be controlled while load is measured

There are a number of issues to be resolved before the use of plastic substrates by the display industry becomes widespread. In particular plastics are much more temperature sensitive than glass. This temperature sensitivity means that low temperature deposition techniques for conducting films and alignment layers

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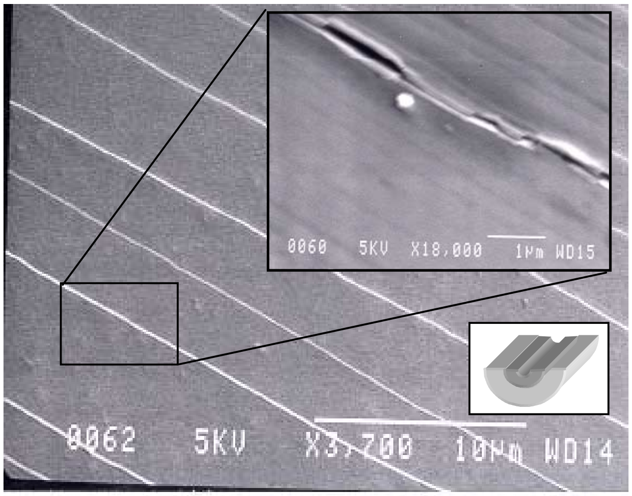

Figure 2 Electron Micrographs of ITO layer in compression showing cracks in the ITO layer.

must be developed. In addition to difficulties in processing due to temperature issues the ITO layer can deteriorate in-service due to mechanical deformation of the substrate. Our previous work has focused on the increase in resistance of the ITO layer by applied stress [17-18]. We have seen that the resistance increases with increasing uniaxial strain and that the increase in resistance is caused by microscopic cracks in the ITO layer. This cracking is also evident in compression and causes an increase in resistance. Typically the resistance was seen to increase for strains greater than 2%. An SEM micrograph of an ITO coated PET sample loaded to 3% in compressive bending is shown in Figure 2.

In this contribution we focuses on the thermal properties of ITO on plastics and relate shrinkage of the PET to increased resistance of the ITO layer. Our ongoing objective is to understand the factors affecting the reliability of Indium Tin Oxide (ITO) coated polymer substrates and to develop reliable conducting substrates for light weight flexible display applications.

Thermal mechanical analysis (TMA) measures the mechanical properties of materials as the materials are deformed under stress at a variety of temperatures [19]. Such measurements provide quantitative and qualitative information about the performance of the materials. DMA can be used to evaluate a wide variety of material types (elastomers, thermoplastics, viscous thermosetting liquids composites coatings and adhesives, ceramics, metals). It is particularly useful for evaluating polymeric materials, which exhibit time and temperature effects on mechanical properties because of their viscoelastic nature [20]. The mechanical properties of brittle coatings such as ITO are dependent on temperature because of these viscoelastic properties [21]

The important components of a TMA are the drive motor (which supplies the deformation to the sample), the drive shaft which transfers the force from the drive motor to the clamps which hold the sample, the displacement sensor (which measures the deformation that occurs under the applied force, the temperature control system (furnace) and the sample clamps. A schematic of a TMA showing the important components is shown in Figure 1.

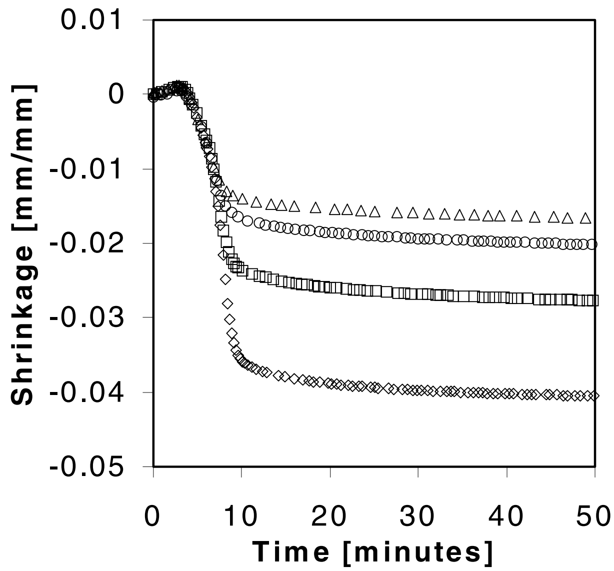

Figure 3 Shrinkage as a function of time-at-temperature for a DuPont 453 PET substrate ◊ 180°, 170° C, ○ 160° and △ 150° C in the machine direction.

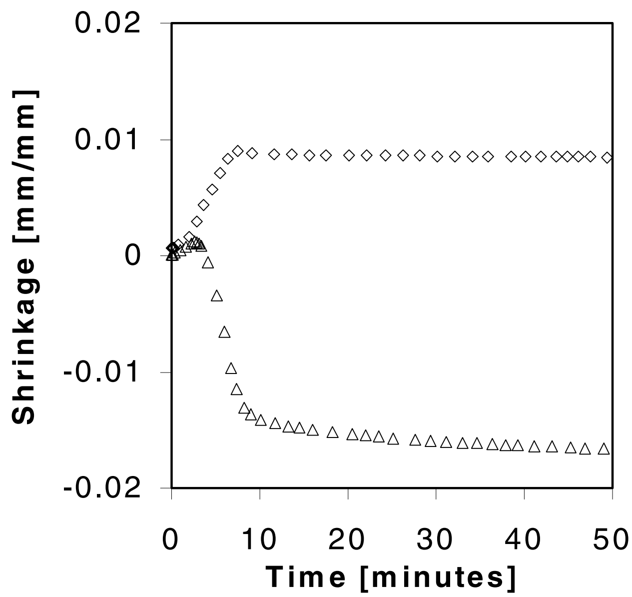

Figure 4 Shrinkage as a function of time-at-temperature for a DuPont 453 PET substrate parallel (△) and perpendicular (◊) to the machine direction.

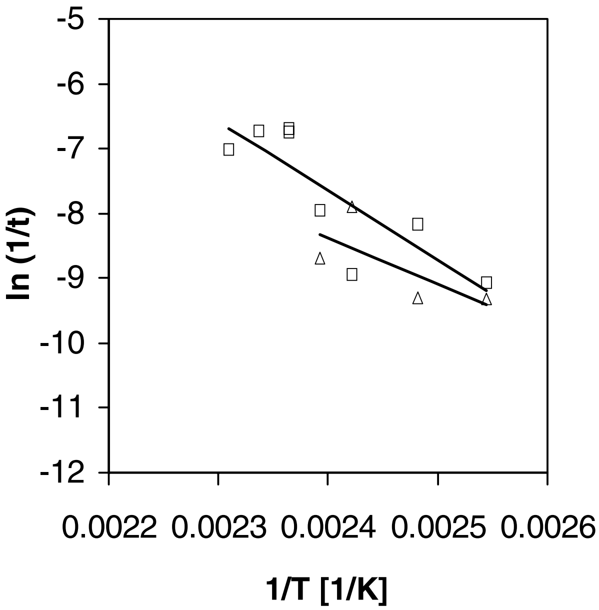

Figure 5 Arrhenius plot for time-at-temperature for a resistance increase of 50% as a function of temperature. Data are shown for similar ITO coatings – 200 Ω/ on different substrates. □ ITO on optical grade PET (DuPont 453), △ heat stabilized PET (DuPont ST-504).

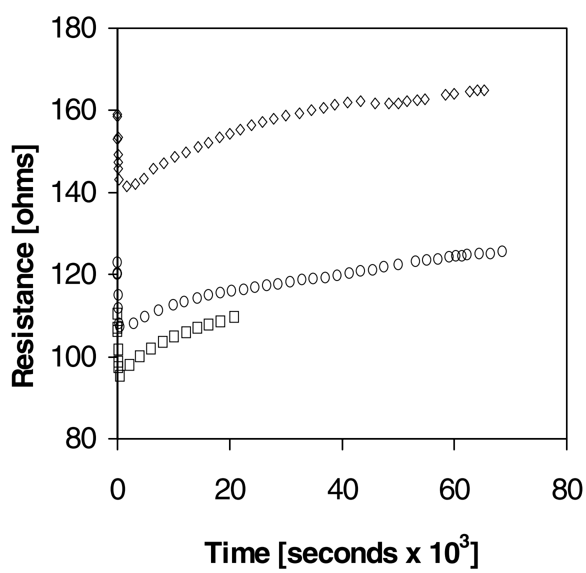

Figure 6 Resistance as a function of time-at-temperature for a 200 Ω/ ITO layer on a DuPont 453 substrate. ◊ 140°, O 150° and 160° C.

Figure 1). A small load is applied to the sample to ensure the film is not buckled. The extension under fixed load can be measured as a function of temperature or the extension can be measured as a function of time at a fixed temperature. In addition the load can be measured as a function of temperature for a fixed displacement.

TMA is an ideal technique for investigating the orientation effects in films. The properties of films are influenced by orientation effects resulting from production of the film. Rolled polymeric films shrink with temperature due to the release of tension built-up during the rolling process.

2. Results

We have measured the shrinkage of ITO coated PET substrates using a Thermal Mechanical Analyzer (TMA). A constant load of 0.5 N was applied to a 12 mm long sample to ensure that it was fully extended – i.e. could not curl. The temperature was then ramped to a test temperature and the shrinkage measured as a function of time. The shrinkage of a PET substrate (DuPont 453) at 150°, 160°, 170° and 180° C is shown in Figure 3. Initially a small amount of thermal expansion occurs followed by severe shrinkage. After approximately 10 minutes the rate of shrinkage decreases and the PET shrinks more slowly. The extent of shrinkage is extremely sensitive to temperature and at 180° C approaches 4% strain (0.04). As reported previously this is comparable with the strain required to cause cracking in the ITO layer [17] and may have a significant effect on the resistance.

The shrinkage of the PET substrate is anisotropic. Similar samples of DuPont 453 were cut in orthogonal directions (parallel and perpendicular to the machine direction of the roll). The machine direction is labeled △ and the orthogonal direction ◊. A graph of the shrinkage at 140° C of a DuPont 453 substrate is shown in Figure 4. In the machine direction the substrate shrinks causing expansion in the orthogonal direction. Shrinkage is often used as a measure of the orientation of polymer films. In a roll-to-roll process there is inevitably stretching in the rolling (machine) direction. At elevated temperatures the oriented polymer chains can relax and shrinkage occurs in the machine direction. If shrinkage is more than 2% it is possible that cracking will occur in the ITO layer thus increasing the resistance.

We have measured the change in resistance of ITO coated PET using a custom built 4-point probe in a temperature enclosure. The resistance was monitored in-situ for a number of hours at a range of constant temperatures. Figure 6 shows the resistance of a 200 Ω/ sample on DuPont 453 as a function of time at three temperatures 140°, 150° and 160°. Initially the resistance drops rapidly and then increases gradually. The change in resistance is more rapid at higher temperatures and is thermally activated. The dependence of the rate of a thermally activated process on temperature is described by an Arrhenius relationship.

$$K = Ae^{\frac{-E_a}{RT}}$$

where K is the rate of the process, E_a the activation energy, R the gas constant, T temperature and A an experimental constant. An Arrhenius plot for the same ITO on two different PET substrates is shown in Figure 5. The squares represent the data for a 200 Ω/ sample on DuPont 453 and the triangles the same ITO on a heat stabilized grade of PET DuPont ST-504.

The slope of the Arrhenius curve is less for the heat stabilized than for the non-stabilized PET. This indicates that the ITO on heat stabilized PET exhibits a lesser dependence of resistance on temperature than is evident for non-stabilized PET i.e. the activation energy of the processes are different. As one might expect the change in resistance with temperature is strongly dependent on the thermal properties of the polymer substrate. The heat stabilized ST504 shrinks less than the DuPont 453 and as a consequence exhibits a lesser dependence of resistance on time-at-temperature.

The dependence of resistance on time-at-temperature must be considered when storing or using devices that utilize ITO on polymer substrates. It is also clear from our results that the substrate plays a very important role in the thermal reliability of flexible display devices. The change in resistance with temperature may also be important during fabrication of devices containing ITO coated polymers.

3. Conclusions

The thermal properties of flexible substrates is an important design consideration in considering the next generation of portable displays in terms of performance and processing. Our results highlight the dependence of shrinkage and resistance on temperature and we have shown that the change in resistance with temperature is a thermally activated process and depends on the thermal properties of the substrate. We will also show that the shrinkage is anisotropic and occurs most strongly in the machine direction.

4. Acknowledgements

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