High Performance Barrier Films via Vacuum Roll Coating

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ABSTRACT

High performance barrier films have been made by a vacuum roll-to-roll coating process. Water vapor and other gas transmission rates have been studied by various methods including tritiated water and calcium coupon testing. Tritiated water vapor transmission rates as low as 10^{-6} g/m^2/day at 22^{o}C were measured for these films. A wide range of barrier performance is possible from this process and water transmission rates can be engineered to a desired level from 10^{-2} g/m^{2}day to 10^{-6}g/m^{2}day, depending on the application. These films have uses for protecting organic electronic devices such as OLEDs.

INTRODUCTION

High-performance, light transmitting, flexible-barrier films have been under development for a number of years [1]. These films are demonstrating a new level of barrier performance not readily seen from available barrier films. In addition to the high barriers to water-vapor and oxygen transmission, these films are defining a new class of advanced barrier materials which are optically transparent and mechanically flexible, see Figure 1. A main driver for the improvement of these high-performance barrier films is their implementation into applications such as organic light emitting diode (OLED) displays [2]. It is speculated that these displays require water vapor transmission rates (WVTR) of 10^{-6} g/m^{2}day [3] while maintaining high optical transparency. While current OLED displays use glass to protect the moisture-sensitive materials, the use of flexible film enables a new approach in both the manufacturing process and the device itself. The flexibility offered by high-performance barrier films is attractive to manufacturers since this could enable cost-effective roll-to-roll manufacturing methods. The replacement of glass in a device provides significant decreases in weight and thickness and could enable the development of next-generation flexible displays. In addition to the traditional OLED-based technologies that require 10^{-6} g/m^{2}day performance, there are emerging display-based technologies which require barrier performance to be less than 10^{-3} but not as low as 10^{-6} g/m^{2}day. These technologies are based on specially formulated OLED device materials [4] and could provide accelerated adoption of advanced barrier film-based products in the display market.

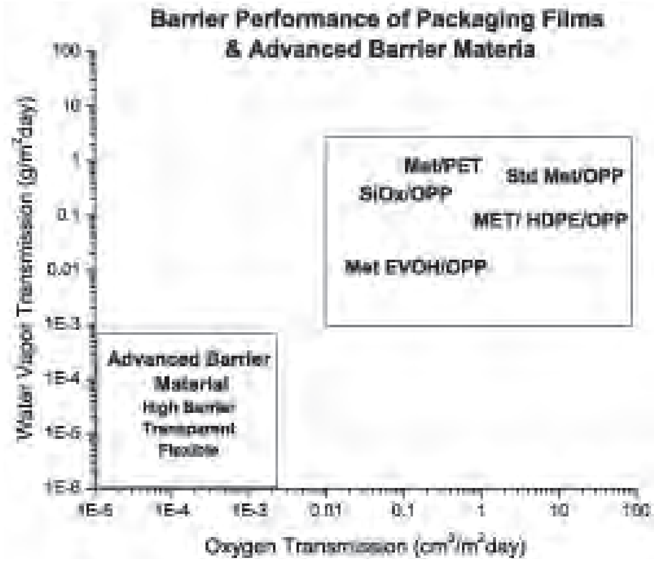

Figure 1: Performance of common barrier films and advanced barrier materials. Met=metallized, OPP=polypropylene, HDPE=high density polyethylene, PET=polyesterteraphthalate, SiO_x=silicon oxide, EVOH=ethylene vinyl alcohol.

This paper discusses barrier film performance results from a unique roll-to-roll barrier coating technology that combines vacuum deposition of polymers and reactively-sputtered materials. The barrier coating technology was first introduced in the early 1990's [5,6]. Subsequent excellent work was carried out using this process by Affinito in 1996 [1,7] and others continue to work with this technology applying it to batch coating systems [8]. Other high barrier roll-coating technologies are also being developed which use plasma-enhanced chemical vapor deposition (PE-CVD) of graded barrier-layers [9] and thick-PE-CVD layers [10] onto flexible substrates.

To utilize barrier films in flexible display applications, a flexible barrier adhesive is required. This paper also presents results on barrier film and adhesive encapsulation systems [11] developed for early-adopter flexible-electronic applications market.

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EXPERIMENTAL

Barrier constructions were made on a vacuum roll coater where polymer and oxide layers were deposited onto a moving web substrate [5,6,12]. Oxide layers were reactively sputtered from 10% aluminum doped silicon targets using dual AC cathodes and polymer layers were deposited by radiation curing monomers condensed on the chilled web. Multi-layers can be built up by repeating the process to the desired number of layers. Water vapor transmission rates were measured at various temperatures using a Mocon Permatran-W-700 instrument [12]. Historical single dyad results from numerous runs and down web positions are shown in Figure 2. Higher numbers of dyad coatings were made and tested using the tritiated-water vapor (HTO-WVTR) test method [13]. This result is shown in Figure 3.

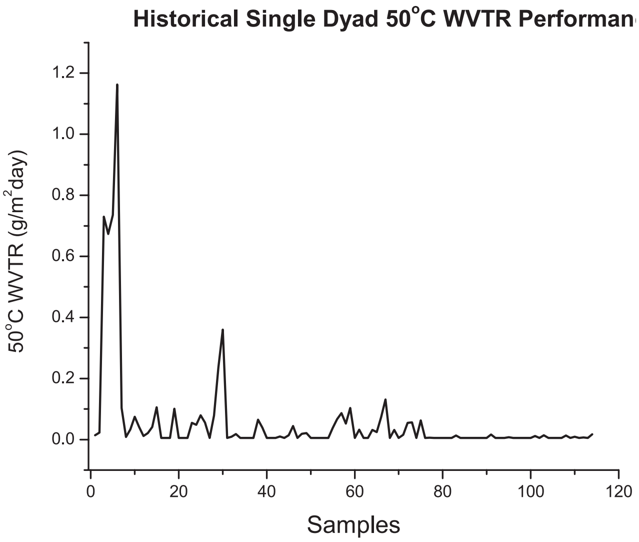

Figure 2: Historical results (Mocon measurements) from numerous runs and down web positions.

Optical transmittance was measured from 350nm to 900nm using a Perkin-Elmer Lambda-900 UV-Vis spectrophotometer. A typical multi-layer barrier film spectrum is shown in Figure 4.

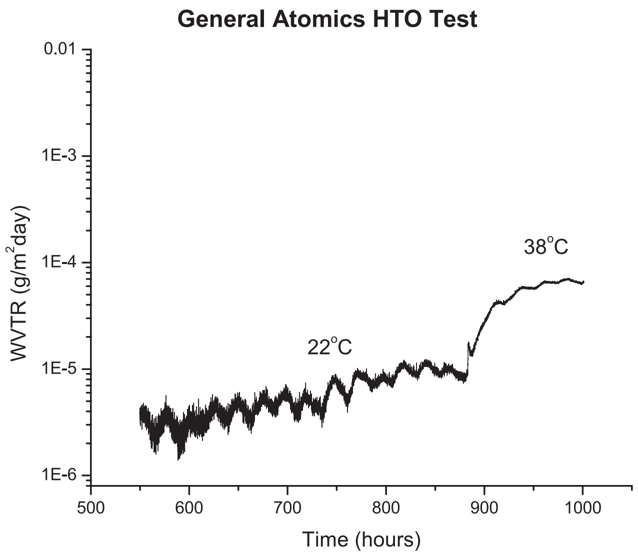

Figure 3: HTO-WVTR measurement made on a multiple dyad barrier film sample demonstrating 10^{-6} g/m^{2}day performance at room temperature [15]. The film was conditioned for 550 hours on the HTO-instrument prior to turning on the HTO detection.

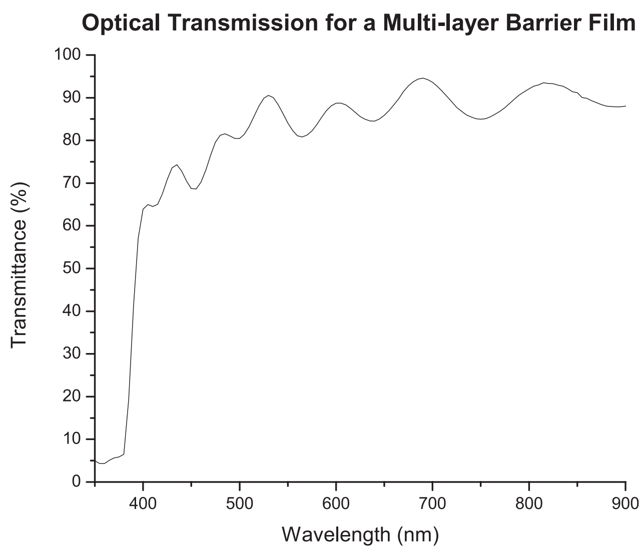

Figure 4: Optical transmittance of a multi-layer barrier film on PEN substrate.

Pressure sensitive adhesives (PSA) and UV curable PSAs were formulated specifically to work with the barrier films presented here. Adhesives were applied to barrier films and evaluated using a calcium test. Briefly, approximately 1000Å of Ca was deposited onto a dried glass substrate by thermal evaporation in vacuum chamber attached to a glove box. The PSA was laminated onto the barrier film sample and dried in a vacuum oven. The laminate barrier/PSA was then applied to the Ca coated glass substrate in the glove box. The barrier film encapsulated Ca/glass sample was then placed into an environmental chamber held at 60°C and 90% relative humidity. Then the optical density of the sample was periodically monitored. The opaque metallic calcium is converted to transparent calcium hydroxide allowing assessment of permeation of moisture into the encapsulated sample. The results are shown in Figure 5. Note: the barrier film construction used in the calcium test shown in Figure 5 was not the same construction as film shown in Figure 3. The film used in Figure 5 was not as high performing but had a WVTR below 0.005 g/m^{2}day at 50°C.

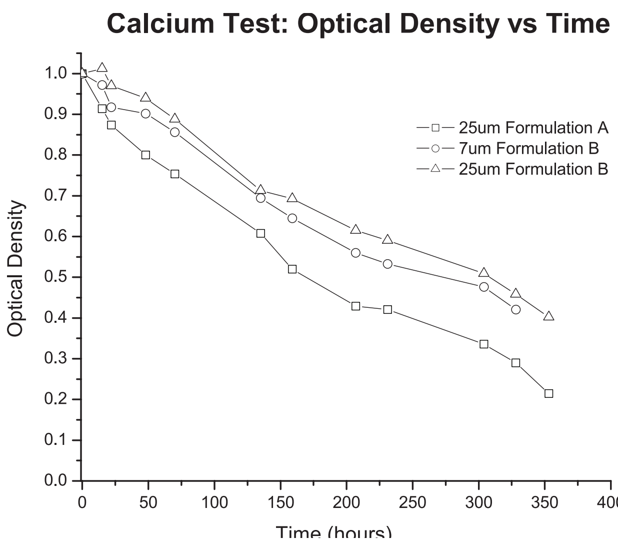

Figure 5: Calcium test data for the same barrier film with varying adhesive formulations and thickness.

Results and Discussion

High barrier performance is required for flexible OLED displays [3,14] as mentioned in the introduction. The polymer sputter coating process presented here has been advanced to the point where significant quantities of high quality barrier film can be made by an efficient roll-to-roll process, see Figure 2. This process can make varying levels of barrier performance from 10^{-2} to 10^{-6} g/m^{2}day, see Figures 2 and 3. As demonstrated by the historical data in Figure 1, the current single dyad process consistently yields single dyad coatings that perform below the detection limit at 50°C (<0.005 g/m^{2}day) of the WVTR instrument. If the historical WVTR of barrier films with more than 1 dyad were plotted as in Figure 1 the result would be a straight line as all the data would be below detection at 50°C on the Mocon instrument. A sample film with more than one dyad was measured by the HTO method [15] at 22°C and shown in Figure 3. The film performed less than 10^{-5} g/m^{2}day for more than 850 hours (after a 550 hour soak) before the temperature of the test was increased to 38°C. After equilibrium was established, the equilibrated HTO rate remained less than 10^{-4} g/m^{2}day. For purpose of discussion, one can estimate an HTO activation energy from the temperature dependant data in Figure 3 [15] and compare it to the activation energy of the bare substrate, in this case PET film. (This activation energy measurement can only be called an estimate since only two data points are available for the analysis where usually 3 or more data points are required. It is also important to note that there may be differences in HTO permeation versus non-tritiated water vapor permeation and this is not studied here. For estimation purposes, activation energy measured with HTO temperature data is assumed to be equivalent to that of non-tritiated water vapor.) Barrier coatings on plastic substrates that have significant defects exhibit activation energies ($E_{a\text{-}barrier}$) for water vapor permeation equal to that of the uncoated substrate ($E_{a\text{-}sub}$) [17]. This indicates the permeation mechanism is still limited by the water-polymer interactions in the substrate. An increased activation energy from a barrier coating, that is, $E_{a\text{-}barrier} > E_{a\text{-}sub}$, indicates a change in permeation mechanism. For the data shown in Figure 3 the estimated water vapor activation energy is about 91kJ/mol. This is significantly higher than the bare PET substrate activation energy of 40 kJ/mol to 50 kJ/mol reported in the literature [10, 15,16].

Barrier films coated with PSA were evaluated using the calcium test as described in the experimental section. Results of monitoring the optical density over time under accelerated conditions of 60°C and 90% humidity show good calcium retention with the barrier-film/PSA laminate construction, see Figure 5. An acceleration factor of 20 to 30x has been observed for this type of calcium test [17]. OLED panel manufactures generally require 500 hour testing at 60°C and 90% RH for their product specification. Rigorous correlation between calcium testing and OLED lifetime testing has not been established. However, in our laboratories we have observed similar operating lifetimes for glass encapsulated and barrier-film/PSA encapsulated OLEDs. These results are an early demonstration of barrier film and adhesive for encapsulating systems for early adopter flexible OLED technology [4].

SUMMARY AND CONCLUSIONS

The barrier film performance presented here demonstrates the readiness of this roll-to-roll process to make a range of barrier performance from ultra-low 10^{-6} g/m^{2}day to the less demanding but challenging 10^{-4} g/m^{2}day while retaining high optical transparency. Significant increase in activation energy of a barrier coated film over the bare substrate suggests that the quality of the barrier film is high, i.e., very few significant defects. The barrier films combined with pressure sensitive barrier adhesive offers unique opportunities for flexible-based electronics needing high performance encapsulation solutions.

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